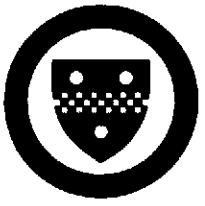
Preprint

SPACE RESEARCH COORDINATION CENTER



University of Pittsburgh

DISSOCIATION OF CH_4 BY ELECTRON IMPACT: PRODUCTION OF METASTABLE HYDROGEN AND CARBON FRAGMENTS

BY

T. G. FINN, B. L. CARNAHAN AND E. C. ZIPF

SRCC REPORT NO. 209

UNIVERSITY OF PITTSBURGH

PITTSBURGH, PENNSYLVANIA

AUGUST 1974

Dissociation of CH_4 by Electron Impact: Production of Metastable Hydrogen and Carbon Fragments

T. G. Finn, B. L. Carnahan and E. C. Zipf

Department of Physics
University of Pittsburgh, Pittsburgh, Pennsylvania 15260

(Journal of Chemical Physics)

Sponsored by

Advanced Research Projects Agency
ARPA Order No. 826
Contract No. DA-31-124-ARO-D-440
(Monitored by: U.S. Army Research Office)

and

National Aeronautics and Space Administration
Grant NGL 39-011-030

August 1974

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY (Corporate author)
University of Pittsburgh
Pittsburgh, Pa 15260

2a. REPORT SECURITY CLASSIFICATION
Unclassified

2b. GROUP

3 REPORT TITLE
Dissociation of CH_4 by Electron Impact: Production of Metastable Hydrogen and Carbon Fragments

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
Scientific paper - August 1974

5 AUTHOR(S) (First name, middle initial, last name)
T. G. Finn, B. L. Carnahan and E. C. Zipf

6 REPORT DATE
August 1974

7a. TOTAL NO. OF PAGES
29

7b. NO. OF REFS
25

8a. CONTRACT OR GRANT NO
DA-31-124-ARO-D-440

b. PROJECT NO

c.
ARPA Order No. 826

d.

9a. ORIGINATOR'S REPORT NUMBER(S)

9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
SRCC No. 209

10 DISTRIBUTION STATEMENT
Approved for public release; distribution unlimited.

11 SUPPLEMENTARY NOTES
MONITORED BY:
U. S. Army Research Office-Durham

12. SPONSORING MILITARY ACTIVITY
ARPA, 1400 Wilson Blvd., Arlington, Va. 22209
NASA Headquarters, Code SL, Washington D. C. 20546

13 ABSTRACT

Metastable fragments produced by electron impact excitation of CH_4 have been investigated for incident electron energies from threshold to 300 eV. Only metastable hydrogen and carbon atoms were observed. Onset energies for the production of metastable hydrogen atoms were observed at electron impact energies of 22.0 ± .5 eV, 25.5 ± .6 eV, 36.7 ± .6 eV and 66 ± 3 eV, and at 26.6 ± .6 eV for the production of metastable carbon atoms. Most of the fragments appear to have been formed in high-lying Rydberg states. The total metastable hydrogen cross section reaches a maximum value of approximately 1×10^{-18} cm^2 at 100 eV. At the same energy, the metastable carbon cross section is 2×10^{-19} cm^2.

DD FORM 1 NOV 68 1473

UNCLASSIFIED

Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Dissociative Excitation						
Methane						
Electron Impact						
Metastable Atoms						
Rydberg States						
Hydrogen						
Carbon						

Dissociation of CH_4 by Electron Impact: Production of Metastable Hydrogen and Carbon Fragments*

T. G. Finn, B. L. Carnahan and E. C. Zipf

Department of Physics

University of Pittsburgh

Abstract

Metastable fragments produced by electron impact excitation of CH_4 have been investigated for incident electron energies from threshold to 300 eV. Only metastable hydrogen and carbon atoms were observed. Onset energies for the production of metastable hydrogen atoms were observed at electron impact energies of 22.0 $\pm$ .5 eV, 25.5 $\pm$ .6 eV, 36.7 $\pm$ .6 eV and 66 $\pm$ 3 eV, and at 26.6 $\pm$ .6 eV for the production of metastable carbon atoms. Most of the fragments appear to have been formed in high-lying Rydberg states. The total metastable hydrogen cross section reaches a maximum value of approximately 1×10^{-18} cm^2 at 100 eV. At the same energy, the metastable carbon cross section is 2×10^{-19} cm^2.

* This research was supported by the Advanced Research Projects Agency of the Department of Defense and was monitored by U. S. Army Research Office Durham under Contract No. DA-31-124-ARO-D-440 and by the National Aeronautics and Space Administration, under Grant NGL 39-011-030.

I. INTRODUCTION

Metastable species play an important role in the ionization balance and thermal economy of a planetary atmosphere; they also contribute significantly to the excitation of radiation in airglow and auroral phenomena. For these reasons,our laboratory has undertaken the investigation of metastable dissociation fragments of molecules that are of aeronomic interest. In previous experiments performed in this laboratory, the time-of-flight technique has been used to investigate dissociation products from such atmospheric constituents as O_2, N_2, CO, CO_2, NO, NO_2 and N_2O[1-8]. In this paper we describe our work on methane which is an important constituent in the Jovian atmosphere and in the terrestrial atmosphere at low altitudes.

The results of this investigation of CH_4 can be summarized as follows. (1) The threshold energy for five different processes in which metastable hydrogen or carbon atoms are produced have been determined in the energy range from 20 to 70 eV. (2) Metastable hydrogen atoms are produced in four of these collision processes and metastable carbon atoms in the other. (3) The first two hydrogen processes are simple two body dissociations in which the CH_3 fragment is left in its ground electronic state. The other two hydrogen processes occur at onset energies so high that the CH_3 fragment must undergo ionization, further dissociation or both. (4) In the hydrogen processes, the kinetic energy of the hydrogen fragments varies from 1 to 7 eV around the threshold regions, and increases to as much as 14 eV at higher impact energies. (5) In the carbon process, a metastable carbon atom in a high-lying Rydberg state is produced with about 1 eV

of kinetic energy along with two hydrogen molecules in the ground electronic state. In addition the onset for the production of energetic UV photons ($h\nu > 5$ eV) is also measured and compared with other results.

II. APPARATUS

The TOF spectrometer used in this experiment has been described elsewhere.[9] It suffices here to describe briefly only the essential components of the apparatus which include an electron gun, a collision chamber, a metastable detector and a set of electrostatic quenching plates. The electron gun, which is pulsed at a rate up to 10^4 Hz, injects the electron beam into the collision chamber at any desired energy up to 300 eV. The integrated beam intensity as monitored by a Faraday cup located at one end of the collision chamber is typically 10^{-7} amperes for a duty cycle of 1%. The metastable particles diffuse out of the collision chamber at an angle of 90 degrees with respect to the electron beam, and impinge on a Cu-Be electron multiplier which serves as the metastable detector and is located at a distance of either 6.4 or 25.9 cm from the collision region. The metastable particles are detected if the energy of the excited state is greater than the work function of the detector ($\phi \simeq 5$ eV). The output pulses of the multiplier are amplified, discrimated and eventually processed by a multichannel analyzer. In addition to metastable particles, UV photons, electrons and ions can also trigger the multiplier. However, a strong magnetic field (150 gauss) which helps to focus the electron beam effectively prohibits the charged particles from reaching the

detector.

In order to distinguish hydrogen atoms in the 2S state from those in other metastable states, we introduced an electrostatic field in the transit region between the collision chamber and the metastable detector. We will demonstrate later that such a field causes the H(2S) to decay while leaving other metastable fragments unaffected. The electric field is produced by two parallel plates located in front of the detector. When the surface detector is located 6.4 cm from the collision chamber, the quenching plates extend from 2.65 cm to 4.65 along the metastable beam path, with a separation of 2.6 cm between them. With the detector at a distance of 25.9 cm the plates extend from 17.1 cm to 24.3 cm along the beam with a separation of 2.7 cm. Electric fields as high as 150 v/cm were maintained across the plates.

The TOF spectrometer was operated in two different modes in this experiment. In the time-to-amplitude conversion (TAC) mode the primary data pulses are fed into a time-to-amplitude converter and then processed by a multichannel analyzer operating in the pulse height analysis mode. In this way time-of-flight spectra were obtained, such as those shown in Figures 1 and 2. In the single channel mode only the data pulses detected within a certain time interval are counted and fed into the multichannel analyzer. This mode was used to obtain the excitation function of the fragments. A voltage ramp from the multichannel analyzer was used to control the electron impact energy. By using the other subdivisions of the multichannel analyzer, we were also able to assign a value of primary electron beam intensity and

apparent impact energy to each channel and thereby convert the apparent excitation function into the actual function such as those shown in Figure 3.

The actual impact energy was determined by observing the onset of the neon metastable at 16.7 eV. Several measurements were taken with a mixture of CH_4 and Ne as the target gas in order to determine accurately the onset energy of the first metastable hydrogen fragment around 22 eV. Because of the overlap in the arrival times of the hydrogen fragments, the onset energies for the production of the fragments around 25, 36 and 66 eV could not be precisely measured. Consequently the threshold energies for those three processes were determined by their appearance in the TOF spectra.

III. RESULTS

A. TOF Spectra and Kinetic Energy

The TOF spectrum of metastable fragments from CH_4 at various electron impact energies is shown in Figures 1 and 2. In the first figure four distinct hydrogen fragments are evident, most of which are formed in high-lying Rydberg states. In the spectrum at 25 eV, there is one fragment visible. The kinetic energy of the fragment is between 1.7 and 3.5 eV. As the electron impact energy increases, another fragment appears which has a kinetic energy between 4 and 7 eV. The cross sections for the two processes continue to increase and reach a plateau around 35 eV where the kinetic energy of the fastest fragment is about 8 eV. In the spectrum taken at 40 eV, the appearance of the

third hydrogen fragment, between the other two peaks is evident. The kinetic energy of this fragment is between 3 and 4.5 eV. When the energy of the incident electron reaches approximately 66 eV, the excitation of the last and most energetic hydrogen fragment begins. The cross sections for the last two processes continue to increase. These processes finally become dominant at higher energies. In the final spectrum shown in Figure 1 (taken at 100 eV), the kinetic energy of the fastest fragments is about 14 eV.

Time-of-flight spectra taken on the 100 μsec TAC are displayed in Figure 2. These spectra show the presence of a slow metastable fragment which we believe to be atomic carbon in a high-lying Rydberg state. The kinetic energy of this fragment is between 1 and 2 eV. It was difficult to identify this fragment because of its low velocity and small cross section. Identification as atomic carbon was accomplished only after comparison with the results of the experiments by Kupriyanov and Perov[10], Aarts et al.[11], and Sroka[12]. The justifications for this conclusion are discussed later.

B. Threshold Energies

1. Vacuum Ultraviolet Photons

The emission spectrum of CH_4 produced by electron impact has been investigated by Aarts et al.[11], Sroka[12], and McGowan et al.[13]. The previous results indicate that most of the UV radiation consists of Lyman α photons with a small amount of other Lyman radiation and carbon lines included. The result of our experiment for the threshold of UV radiation ($\lambda < 2400$) is 21.1 $\pm$ .5 eV. This value is in good

agreement with the results of Sroka for the onset of Lyman α (20.7 ± .8 eV) and consistent with the work of Aarts et al. who observed the onset of Balmer α excitation at 21.9 ± .5 eV.

2. Metastable Hydrogen Fragments

There have been two previous investigations of the metastable fragments produced by electron impact excitation of CH_4. Clampitt[14] has reported the onset for metastable hydrogen fragments at an impact energy between 19 and 21 eV. In addition, Kupriyanov and Perov[10] found the onset for the production of hydrogen atoms in Rydberg orbitals in this same energy region. We have observed the onsets for hydrogen fragments at impact energies of 22.0 ± .5 eV, 25.5 ± .6 eV, 36.7 ± .6 eV and 66 ± 3 eV. These results can also be favorably compared with the onset energy for the production of H^+ from electron impact on CH_4. Smith[15] found the appearance potential for H^+ ions at 22.7 eV and recently, Appell and Kubach[16] observed H^+ ions with kinetic energies between 1.4 and 3.4 eV at an onset energy of 24.0 ± .5 eV.

3. Metastable Carbon Atoms

The onset for the excitation of metastable carbon atoms was observed at an impact energy of 26.6 ± .6 eV. Kupriyanov and Perov[10] performed the only other methane experiment in which metastable carbon atoms were detected. They observed the threshold energy for the production of carbon atoms in Rydberg states to be between 25 and 30 eV. However, the results of two other experiments can be correlated with the present

results. First, Smith measured the onset of carbon ions to be at an impact energy of 26.7 $\pm$ .5 eV. Second, Sroka[12] found the onset for two UV carbon lines, (the $^3P \rightarrow {}^3P$ 1657 Å and the $^3D \rightarrow {}^3P$ 1561 Å lines) between 26 and 27 eV. Hence the results of other experiments also confirm that highly excited carbon atoms begin to appear around this energy.

C. Effect of the Quenching Plates

The purpose of the quenching plates is primarily to determine whether or not the metastable hydrogen fragments are in the 2S state. A field as low as 20 volts/cm can perturb a hydrogen atom in the 2S state so that the excited atom's lifetime is 1 μsec rather than 1/7 sec for a field free region.[17] On the other hand, a high lying Rydberg is virtually unaffected by an electric field of this magnitude. For example, the n = 20 level has a field free lifetime ranging from 2×10^{-6} sec to 2×10^{-4} sec [18], depending on the angular momentum of the state. For the same n = 20 level, the stark lifetime varies from 1×10^{-5} for M = 0 to 1.5×10^{-4} for M = 18, where M is the third quantum number in parabolic coordinates. In effect, radiative lifetimes for high Rydbergs are only slightly modified by the presence of an electric field. At the same time, the probability of autoionization at the low field strengths of this experiment are negligible.[19] Since the transit time through the quenching field of the hydrogen fragments is a few microseconds, the intensity of the fragments in the 2S state will be greatly attenuated, but those in high lying Rydberg states will not. Hence the quenching

plates can be used to determine approximately the quantum number of the excited state.

Applying the electric field across the molecular beam had different effects on the carbon and hydrogen fragments. The slow carbon fragments appeared to be unaffected by the electric field at any strength. As for the hydrogen fragments, their intensity decreased by approximately 15% when a field of 20 v/cm was applied, but remained virtually unaltered at higher field strengths. From these results we can draw two important conclusions. First, if the carbon fragments are formed in Rydberg states, the quantum number of the states must be large ($n > 20$) because the lifetime of the fragments in the electric field is long compared to the transit time. Second, the hydrogen fragments are formed predominantly in high lying Rydberg states. However, a significant fraction of the fragments are in the 2S state when they reach the quenching region. Either they are formed in the 2S state directly or, more likely, they are formed initially in Rydberg states that cascade to the 2S state before reaching the quenching area.

It is possible to estimate the range of principle quantum numbers for the hydrogen Rydberg fragments. By using the quenching field, we can eliminate the H(2S) component of the metastable beam. A time-of-flight distribution taken with the H(2S) component eliminated shows only Rydberg states. An average lifetime for the Rydbergs can be computed by comparing two such distributions obtained at two distances. Using the results of Hiskes et al.[18] we can then convert the computed lifetime into a range of possible quantum states.

From our experimental results we estimate the average lifetime to be 1.5 to .5 x 10^{-5} sec which implies a range of n = 10 to n = 20 for the principle quantum number of the hydrogen Rydberg fragments.

D. Magnitude and Energy Dependence of the Cross Sections

The relative cross sections from threshold to 300 eV for excitation of UV photons, metastable hydrogen and metastable carbon are shown in Figure 3. As can be seen in the figure, the energy dependence of the cross sections are similar in that they reach a maximum around the same energy, that is, between 80 and 100 eV, and then decrease slowly with energy at approximately the same rate. Only the cross section for the excited carbon fragment shows structure. The metastable carbon cross section rises sharply from threshold and reaches a relative maximum around 40 eV. In this energy range an additional excitation process begins that ultimately becomes the dominant process for production of the carbon fragment at higher energies.

The absolute cross sections for the production of the atomic H and C fragments can be estimated from the parameters of the experiment. However a complication arises in estimating the hydrogen fragment cross sections because the metastable beam consists of atoms in the 2S state as well as in high-lying Rydberg states. This difficulty can be overcome by applying a small electrostatic field (20 v/cm) across the quenching plates to eliminate the H(2S) component. In this way we can measure the cross sections for both the H(2S) fragments and the Rydberg fragments as well. Using the yields for metastable atoms and

molecules as measured by Borst[20], and our own estimate of the lifetime of the Rydberg fragments, we calculate the cross sections at an incident energy of 100 eV and an angle of 90 degrees to be 3×10^{-19} cm^2 for the H(2S) fragments, 1×10^{-18} cm^2 for the H Rydberg fragments and 2×10^{-19} cm^2 for the carbon fragments. For the last cross section we assumed that the excited electron in the carbon atom is in a Rydberg state near the ionization limit of 11.3 eV. The values of the cross sections presented here are only estimates because the angular dependence of the cross sections are not known. Apart from the possible anisotropy in the differential cross sections, there is a factor of two uncertainty in the results.

In an ultraviolet emission experiment, Vroom and De Heer[21] measured the cross section for production of H(2S) fragments by electron impact excitation of CH_4 over the energy range from 50 to 6000 eV. The H(2S) atom was observed by quenching the metastable fragment in an electrostatic field as large as 120 v/cm[22] and then detecting the emitted Lyman α photon. At 100 eV, their value for the H(2S) cross section is 1.0×10^{-18} cm^2 which is larger than our value of 3×10^{-19} cm^2. One possible reason for the discrepancy is that quenched Rydberg fragments contribute significantly to the apparent H(2S) cross section. We estimate that at the electric field strengths employed by Vroom and De Heer, the number of H Rydberg fragments which are quenched and thus can lead to Lyman α radiation is approximately equal to the H(2S) cross section. Thus, the "apparent" H(2S) cross section of Vroom and De Heer includes the contribution of Rydberg fragments which do not necessarily decay via the 2S state.

Strictly speaking, we have probably underestimated the H(2S) cross section because we have not included the cascade contribution from high-lying Rydberg states. Since the Rydberg cross section is much larger than 2S cross section, the number of Rydberg fragments which eventually reach the 2S level is not negligible. However, because the lifetime of the Rydberg fragments is long and only slightly affected by the electrostatic quenching field, most of the Rydberg fragments will collide with the walls or drift out of the field of view before decaying. Hence a significant fraction of the total 2S cross section is not observable in a conventional emission experiment. This difficulty may arise in other experiments which measure resonance radiation from dissociative excitation. Thus, one must be particularly cautious when using laboratory measurements of dissociative excitation emission cross sections in the analysis of upper atmospheric optical data because the laboratory measurements may severely underestimate the total emission cross section that applies when wall collisions and transit time limitations are negligible.

IV. DISCUSSION

A. Production of Metastable Hydrogen Fragments

Four distinct processes have been found in which metastable hydrogen fragments in high-lying Rydberg states are produced when methane dissociates as a result of electron impact. Only the first two hydrogen processes have been uniquely determined and they

correspond to the two body reaction:

$$CH_4^* \rightarrow H^* + CH_3 \qquad (1)$$

where the CH_3 fragment is in the ground electronic state.

In the first hydrogen process, which has an onset at 22.0 eV (see Table I), the energetic fragment has as much as 3.7 eV of kinetic energy. The only reaction possible for this process is the two body process mentioned above. In this case, the total electron energy is distributed as follows: approximately 4 eV for the total kinetic energy, 4.4 eV to sever the bond and 13.5 eV in the form of electronic energy needed to excite the Rydberg state. The second hydrogen process, which begins at 25.5 eV, is similar except that the total kinetic energy is 7.5 eV. The dissociation limit for these two processes is thus the same, 18 eV, and is very close to the first ionization dissociation limit (18.1 eV). The similarity between the ionization dissociation limit and the Rydberg dissociation limit is predicted from the ion core model discussed in Section C.

The reactions corresponding to the last two hydrogen processes cannot be uniquely determined because the threshold energies ($36.7 \pm .6$ eV and 66 ± 3 eV, respectively) are too large to result in the formation of CH_3 into its ground electronic state alone. Instead the CH_3 fragments must be in excited states which probably subsequently dissociate. In the third process, after allowing for the observed kinetic energy of the fragments, for the bond energy and finally for the excitation energy of the hydrogen atom, there are

still 13 eV which are unaccounted for. Similarly, in the last process there are almost 40 eV unaccounted for.

In an attempt to understand the dissociation process more clearly, we substituted CD_4 as the target gas. According to conservation of momentum and energy, when this substitution is made the ratio of the velocity of the H fragment to that of the deuterium fragment in the two-body reaction, $CH_4 \rightarrow CH_3 + H$, is 1.44. The experimental results were that all of the deuterium fragments were shifted approximately the same factor and in reasonable agreement with the predicted value of 1.44. However, there was a slight difference between the shifts of the fragments produced in the first two processes, which are definitely two body reactions, and the shift of the fragments observed for hydrogen processes three and four. This difference suggests that the last two processes (3 and 4) are not two body reactions, but result in multiple fragments (3 or more).

B. Production of Metastable Carbon Fragments

The slow fragment which has a threshold energy of 26.6 eV has not been uniquely identified but there is strong evidence to suggest that it is a carbon atom in a high-lying Rydberg state. Initially, because of the small cross section for the process, we were concerned that the fragment might result from the presence of an impurity in the gas or from a second order process. In order to verify that the fragment was not due to an impurity, four different grades of CH_4 (including research grade in which the largest impurity was less than 35 ppm) were used as the target gas. In each case the slow fragment

was present and its cross section relative to the fast hydrogen fragments was constant and independent of the grade of gas. We were also concerned that the fragment could result from a second order process in which one of the dissociated fragments reacted with the CH_4 in the collision chamber. However, the linear dependence of the slow fragment intensity on the collision chamber pressure and the primary electron beam current indicated that the fragment resulted in fact from a first order process.

After we established that the fragment resulted from direct excitation of CH_4 by electron impact, we attempted to determine its identity. Because of the small energy of the fragment, it could not be uniquely related to a particular process. When CD_4 was substituted as the target gas, the arrival time of the fragment decreased slightly, that is, the fragment velocity increased. Since the arrival time decreased rather than increased, the fragment must be a heavy particle and cannot be atomic or molecular hydrogen. Unfortunately, the overlap of the deuterium fragments was so great that the actual arrival time of the slow fragment could not be precisely determined. However, by measuring the distribution at two different distances, we did determine that the lifetime of the slow fragment is approximately 100 microseconds.

There is evidence which suggests that the slow fragment is atomic carbon in a Rydberg state. Perhaps, the strongest argument is based on the similarity between our TOF results and that of Kupriyanov and Perov[10], who also observed highly excited carbon and hydrogen atoms in an electron impact experiment on CH_4. Their apparatus consisted of two

chambers, one of which served as the collision chamber where the CH_4 was excited, while the other contained the detector, an ion mass spectrometer. Electrostatic and magnetic fields were used to prevent charged particles from escaping the collision chamber. As the neutral atoms and molecules exited the collision chamber, those in high-lying Rydberg states were ionized near a metal surface and detected by the mass spectrometer. Their experiment allowed the unique determination of the excited species by the mass spectrometer, but did not have the time-of-flight aspect that our apparatus possesses.

The similarities between our results for the slow fragment and their results for highly excited carbon atoms are the following. First, the only fragments observed by Kupiyanov and Perov that result from a first order process are highly excited hydrogen and carbon atoms. Second, the cross section for the carbon fragment is much less than that for the hydrogen fragments, just as in the present experiment where the slow fragment cross section is much less that the hydrogen fragment cross section. Third, the onset for the production of highly excited carbon fragments (between 25 and 30 eV) is in good agreement with our result for the slow fragment (26.6 eV). Fourth, their energy dependence for the carbon fragment cross section is similar to that of the slow fragment, that is, the carbon fragment excitation cross section rises sharply from threshold and reaches a relative maximum around 40 eV then continues to increase to an absolute maximum around 100 eV just as the slow fragment cross section in Figure 3.

There are other experimental results which support the hypothesis

that the slow fragment is actually atomic carbon in a Rydberg state. In an ultraviolet emission experiment, Sroka[12] observed, in addition to the Lyman series, the production of two carbon lines at 1657Å ($2p^3s\ ^3P \rightarrow 2p^2\ ^3P$) and 1561Å ($2s2p^3\ ^3D \rightarrow 2p^2\ ^3P$). A similar experiment was performed by Aarts et al.[11]. The onsets for the two carbon lines observed by Sroka (26.2 and 27 eV, respectively) are very close to our onset energy for the slow fragment (26.6 eV) and the energy dependence of the cross section for the 1561Å line is similar to the slow fragment cross section of Figure 2. In an early electron impact experiment on CH_4, Smith[15] observed the production of ions of H, CH, CH_3, H_2 and C. The carbon ion threshold was at 26.7 eV. The significance of the ultraviolet and ion results is that they indicate that around 26 eV carbon atoms in highly excited states begin to appear. In the next section we discuss the reason why it is not surprising to find approximately the same onset for ions, excited states, and high-lying Rydberg states of the same species.

The most likely process for the carbon fragment is $CH_4^* \rightarrow C^* + 2H_2$. From conservation of linear momentum, we estimate that the minimum kinetic energy released in this process is 4.4 eV. This estimate requires that the reaction occurs colinearly, that is, that the two hydrogen molecules travel directly opposite to the carbon atom. If there is an angle between the two hydrogen molecules, then the value of the minimum kinetic energy released must increase. In order to remove two hydrogen molecules from CH_4, 8.3 eV of energy are required. The amount available for electronic excitation is then 26.6 - (4.4 + 8.3) = 13.9 eV. The ionization potential of carbon is 11.3 eV.

If we assume that the metastable state is a Rydberg near the ionization limit, then there are approximately 3 eV unaccounted for which can be channeled into extra kinetic or vibrational energy for the hydrogen molecules. However, if we assumed that the process was $CH_4^* \rightarrow C^* + H_2 + 2H$, then an additional 4.5 eV would be required to dissociate one of the hydrogen molecules. The amount available for electronic excitation would be 9.5 eV. Although the detector could be triggered by a state of this energy, there is no known metastable state in carbon which has this energy and also a lifetime of approximately 10^{-4} sec, which is the lifetime of the state that we estimate from our data.[23]

Finally, let us summarize the reasons for concluding that the slow fragment is atomic carbon in a Rydberg state. First, our laboratory results indicate that the slow fragment is a real first order feature of the time-of-flight spectrum of methane, and is not due to an impurity or a second order effect. Second, experiments conducted with CD_4 as the target gas show that the slow fragment must be a heavy particle, that is, it must consist of at least a carbon atom. Third, in a similar electron impact experiment, Kupriyanov and Perov observed highly excited carbon atoms which had a similar onset, energy dependence, and cross section as the slow fragment that we observe. Fourth, other experimental results indicate that in the energy range where the slow fragment first appears, highly excited carbon atoms also begin to appear. Fifth, the lifetime of the slow fragment that we estimate from our data (10^{-4} s) is larger than that of any of the known metastable states of carbon, hence the state is

likely to be a Rydberg state.

C. The Ion Core Model

Much of the data presented in this paper can be interpreted in terms of the ion core model which was suggested by Kupriyanov[24] and has been extensively developed by Freund[25]. In this model the high-lying Rydberg electron is treated as a "spectator" orbiting the molecule at a large distance while the ion which remains as the "core" of the molecule determines the dissociation processes and products. Initially, the ground state electron is excited to a level of a Rydberg series which converges to any one of several ionization limits. The expectation value <r> of the orbital radius of the Rydberg electron is characteristically very large. Since the electron is so far removed from the nuclei, the remainder of the molecule can be treated as a singly ionized point charge. If the molecule dissociates, the Rydberg electron can be attracted to the positive ion fragment and may end up as a Rydberg electron orbiting this fragment. Otherwise, the parent molecule undergoes dissociative ionization. Hence it is clear in this model why positive ions, excited states and Rydberg states of the same species appear at approximately the same energy with similar excitation functions. In some events, the attraction of the positive ion fragment is not sufficient to capture the electron and the ion is formed. In other cases, where the high-lying Rydberg fragment is formed, the Rydberg electron cascades down to some lower state and produces the observed ultraviolet radiation.

Prior to dissociation, the electronic structure of the molecular

core corresponds closely to that of the singly charged ion. Hence the characteristics of the dissociation process should be determined by the repulsive potential curves of the ion rather than the neutral molecule. Therefore, there should be a strong correspondence between the Rydberg dissociation processes and the dissociative ionization processes in which the ions are formed directly rather than by autoionization. There should be similarities between the two sets of processes with respect to quantities such as threshold energy, dissociation limit and fragment kinetic energy.

There have been only a few experiments in which dissociative ionization by electron impact on CH_4 has been investigated. However, the results of these experiments compare favorably with our results, as predicted by the ion core model. The first electron impact experiment on CH_4 in which ions were detected was performed in 1937 by Smith who observed the production of ions of H, C, CH, CH_3 and H_2 [15]. Smith found the onset for H^+ ions at an incident electron energy of $22.7 \pm .5$ eV. This value is close to our result for Rydberg hydrogen production ($22.0 \pm .5$ eV) and supports the ion core model.

Recently Appell and Kubach have investigated the kinetic energy of protons produced by dissociation of CH_4 [16]. At an incident electron energy of 24 eV, they observe a proton fragment with kinetic energy between 1.4 and 3.4 eV. This process corresponds to the hydrogen fragment which we observe at an onset of 22 eV (see Table I). At an incident energy 4 eV above the first threshold, they observe another process which is similar in two respects to our second H process at 25.5 eV. First, the kinetic energy of the proton and the Rydberg

hydrogen atom are the same, namely, 4 to 7 eV and secondly, the cross section for the second proton is much less than that for the first process just as in our results (see Figure 1). However, Appell and Kubach observe a slow proton with energy between zero and one eV which does not correspond to any of our processes.

There are other similarities between our results and those of Appell and Kubach. The $\tilde{A}\ ^2A$, state of CH_4^+, which lies 22.4 eV above the CH_4 ground state, has been identified as the state correlated with the dissociative ionization process:

$$CH_4 + e \rightarrow CH_4^+ (\tilde{A}\ ^2A) \rightarrow CH_3(X) + H^+ \qquad (2)$$

In the ion core model this state would also be correlated with the dissociation of CH_4 leading to excited hydrogen atoms in Rydberg states (Equation (1)). The dissociation limit observed by Appell and Kubach is 18.1 eV. This limit corresponds to the process:

$$CH_4 \rightarrow CH_3(X) + H^+ \qquad (3)$$

in which the dissociation energy of CH_4 is 4.5 eV and the ionization potential of hydrogen is 13.6 eV. The limit of 18 eV is the same that we obtain for the first two hydrogen processes.

The only data available on C^+ and the other ions is the work of Smith[15]. The onset for C^+ was measured to be 26.7 eV which agrees very well with our result of 26.6 eV. There is no data available on the kinetic energy of the C^+ ions with which to compare our TOF results.

The fact that other ions were observed by Smith but no corresponding Rydberg fragments were observed in TOF spectra is puzzling. However, this fact can be explained if the other ions are formed by autoionization rather than direct excitation.

Table I: Summary of Dissociation Processes, CH_4

Threshold Energy (eV)	Process	Kinetic Energy of Fragment Near Threshold	Minimum K.E. Released	Internal or Electronic Energy
1. 21.1 ± .5 eV	$CH_4^* \rightarrow CH_3 + H^*(2P)$			$\geq$ 10.2 eV
2. 22.0 ± .5 eV	$CH_4^* \rightarrow CH_3 + H^*(R)$	1.7 - 3.7 eV	4.0	13.6 eV
3. 25.5 ± .6 eV	$CH_4^* \rightarrow CH_3 + H^*(R)$	3 - 7 eV	8	13.1 eV
4. 26.6 ± .6 eV	$CH_4^* \rightarrow C^*(R) + 2H_2$	1 - 2 eV	> 4.4	< 13.9 eV
5. 36.7 ± .6 eV	$CH_4^* \rightarrow H^*(R) + ?$	3 - 4 eV	$\geq$ 5	< 28 eV
6. 66. ± 3 eV	$CH_4^* \rightarrow H^*(R) + ?$	5 - 10 eV	$\geq$ 11	< 50 eV

References

1. W. L. Borst and E. C. Zipf, Phys. Rev. A 4, 153 (1971).
2. W. C. Wells, W. L. Borst and E. C. Zipf, Chem. Phys. Letters 12, 288 (1971).
3. W. C. Wells and E. C. Zipf, Phys. Rev. A 9, 568 (1974).
4. W. C. Wells, W. L. Borst and E. C. Zipf, Proc. ICPEAC VII, North-Holland Publishing Co. (Amsterdam, 1971), p. 576.
5. W. C. Wells. W. L. Borst and E. C. Zipf, Trans. Am. Geophys. Union, 52, 878 (1971).
6. W. C. Wells, W. L. Borst and E. C. Zipf, Bull. Am. Phys. Soc., 17, 397 (1972).
7. W. C. Wells, W. L. Borst and E. C. Zipf, J. Geophys. Res., 77, 69 (1972).
8. W. C. Wells and E. C. Zipf, to be published.
9. W. L. Borst and E. C. Zipf, Phys. Rev. A 3, 979 (1971).
10. S. E. Kupriyanov and A. A. Perov, Khim. Vys. Energ. 3, 306 (1969).
11. J. F. M. Aarts, C. I. M. Beenakker and F. J. De Heer, Physica 53, 32 (1971).
12. W. Sroka, Z. Naturforsh. 24a, 1724 (1969).
13. J. W. McGowan, J. F. Williams and D. A. Vroom, Chem. Phys. Letters 3, 614 (1969).
14. R. Clampitt, Polymer 10, 721 (1969).
15. L. G. Smith, Phys. Rev. 51, 263 (1937).
16. J. Appell and C. Kubach, Chem. Phys. Letters 11, 486 (1971).
17. H. Bethe and E. E. Salpeter, Encyclopedia of Physics (Springer-Verlag,

Berlin, 1957) Vol. XXXV p. 372.

18. J. R. Hiskes, C. B. Tarter and D. A. Moody, Phys. Rev. 133, A424 (1964).

19. D. A. Bailey, J. R. Hiskes, and A. C. Riviere, Nucl. Fusion 5, 41 (1965).

20. W. L. Borst, Rev. Sci. Instr. 42, 1543 (1971).

21. D. A. Vroom and F. J. De Heer, J. Chem. Phys. 50, 573 (1969).

22. D. A. Vroom and F. J. De Heer, J. Chem. Phys. 50, 580 (1969).

23. W. L. Wiese, M. W. Smith, and B. M. Glennon, Natl. Std. Ref. Data Series, NBS (U.S.) 1, (1966).

24. S. E. Kupriyanov, Zh. Eksp. Teor. Fiz. 55, 460 (1968) (Sov. Phys. JETP 28, 240 (1969)).

25. R. S. Freund, J. Chem. Phys. 54, 3125 (1971); K. C. Smyth, J. A. Schiavone, and R. A. Freund, J. Chem. Phys. 59, 5225 (1973).

Figure Captions

Figure 1. The time-of-flight spectrum of metastable hydrogen fragments from methane at various electron impact energies. There are four distinct processes. Most of the fragments are formed in high-lying Rydberg states. The distance between the collision center and the detector was 6.4 cm.

Figure 2. The time-of-flight spectrum of metastable carbon fragments from methane at various electron impact energies. The distance between the collision center and the detector was 6.4 cm.

Figure 3. The excitation cross sections for different processes in methane.

A. Dissociative excitation of metastable carbon fragments.

B. Dissociative excitation of metastable hydrogen fragments.

C. Excitation of vacuum ultraviolet radiation. The carbon metastable cross section (A) shows structure around 40 eV.

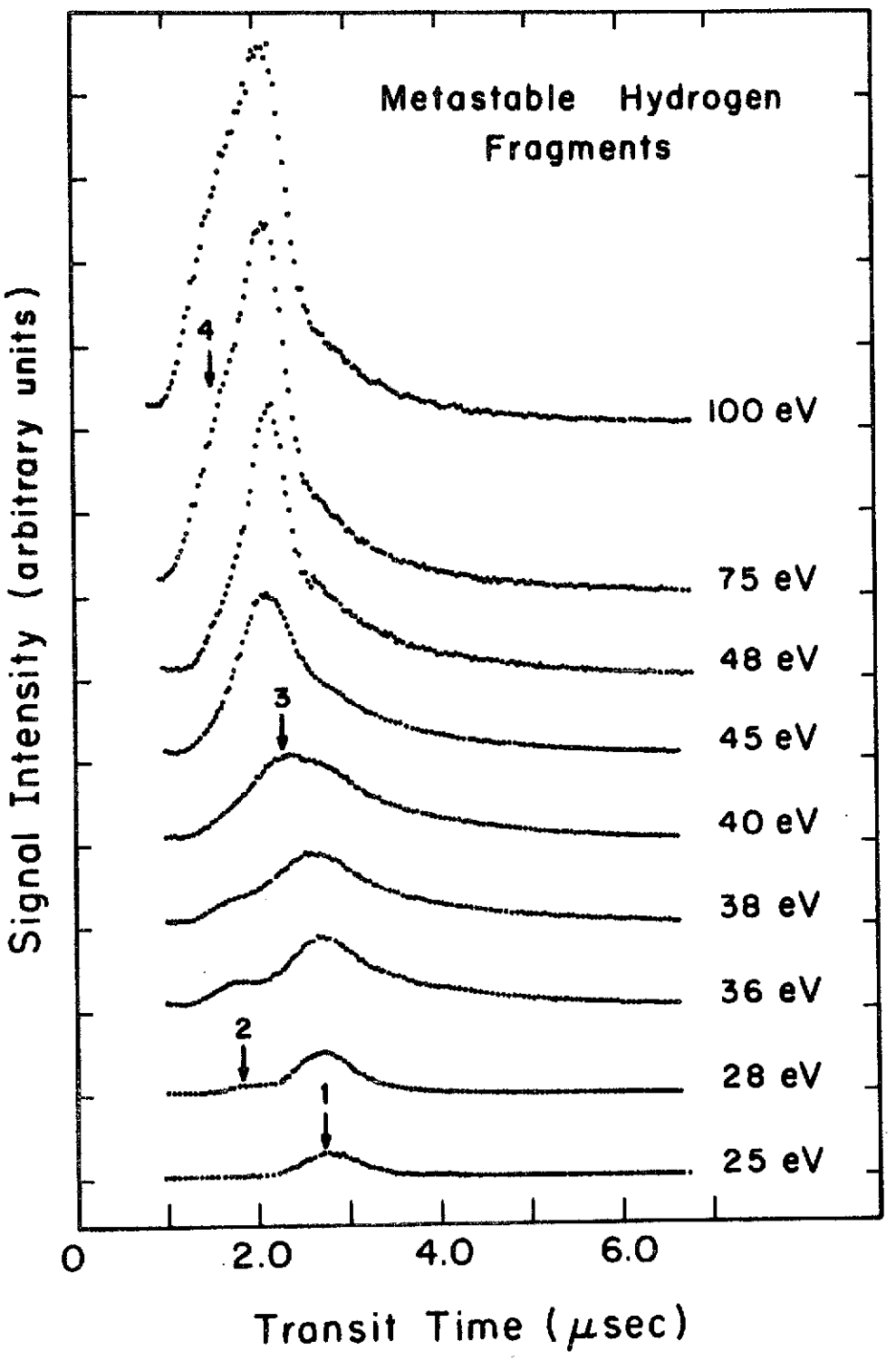

Metastable Hydrogen
Fragments
Signal Intensity (arbitrary units)
100 eV
75 eV
48 eV
45 eV
40 eV
38 eV
36 eV
28 eV
25 eV
4
3
2
1
0
2.0
4.0
6.0
Transit Time (μsec)

Figure 1

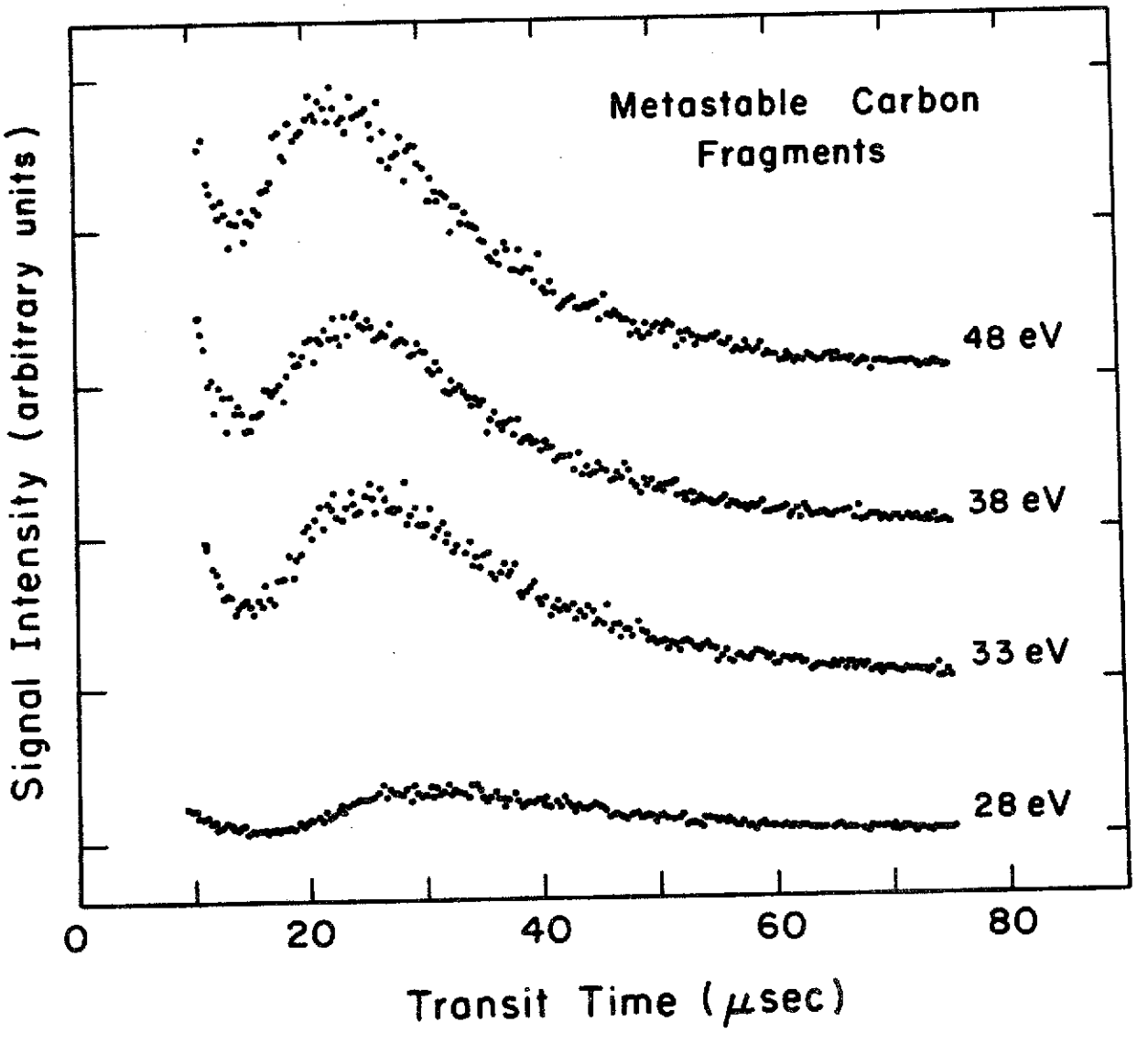

Metastable Carbon
Fragments
48 eV
38 eV
33 eV
28 eV
Signal Intensity (arbitrary units)
0
20
40
60
80
Transit Time (μsec)

Figure 2

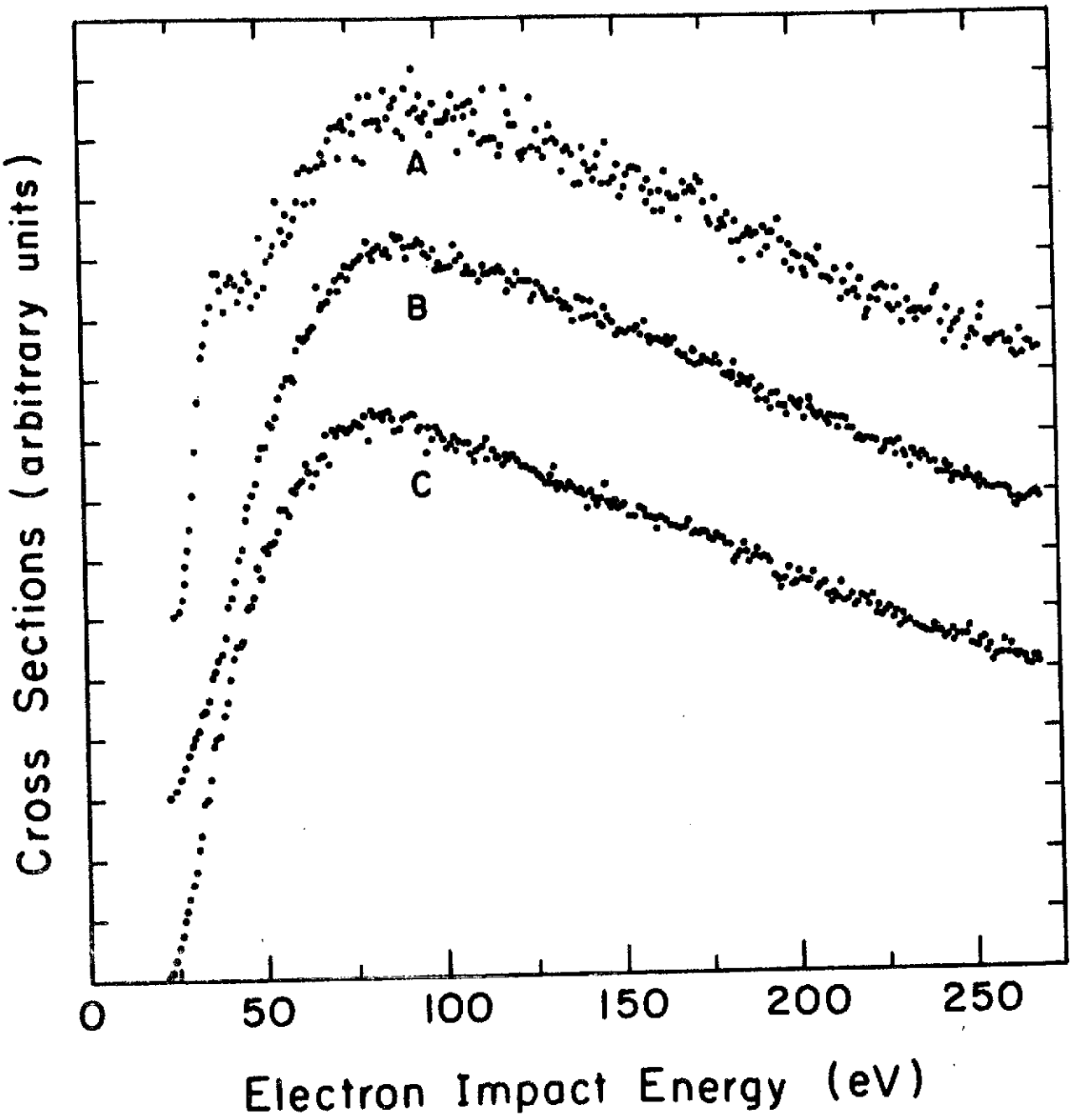

Cross Sections (arbitrary units)
A
B
C
0
50
100
150
200
250
Electron Impact Energy (eV)

Figure 3