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Synergistic Methane Formation on Pyrolytic Graphite Due to Combine H^+ Ion and H^0 Atom Impact

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CFFTP will sponsor research development and studies to extend existing experience and capability gained in handling tritium as part of the CANDU fission program. It is planned that this work will be in full collaboration and serve the needs of international fusion programs

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SUMMARY

Exposure of graphite to multispecies hydrogenic impact, as is the case in tokamaks, could lead to synergistic mechanisms resulting in an enhancement of methane formation, and consequently in increased carbon erosion. We present results obtained in controlled experiments in our laboratories in Toronto and Jülich for the synergistic methane production due to combined sub-eV H^0 atom and energetic H^+ ion impact on pyrolytic graphite. Flux densities were 10^{14}-2×10^{16} H^0/cm^2s for the sub-eV H^0 atoms and 6×10^{12}-5×10^{15} H^+/cm^2s for H^+ ions of 300 eV to 2.5 keV energy. Synergistic factors (defined as the ratio of methane formation rate due to combined H^0 and H^+ fluxes to the sum of the formation rates due to separate species impact) ranged from about 1.5-15 for the experimental parameters used. In addition, a spectrum of formed hydrocarbons in the synergistic reaction of H^+ and H^0 on graphite is presented.

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1. INTRODUCTION

The extensive use of carbon in current fusion devices and its planned use in future machines warrant a comprehensive assessment of the chemical erosion characteristics of carbon when exposed to multispecies impact, as is the case in tokamaks. Recent results, obtained in Jülich [1] and Toronto [2], on the methane production due to simultaneous bombardment of carbon by energetic H^+ ions and sub-eV H^0 atoms (simulating Franck-Condon atoms) show the existence of synergistic effects leading to a significant increase in the methane yield. Although both sets of data show an enhancement in the methane yield, the use of different parameter ranges (e.g., H^+ energy and flux, H^0 flux, etc) does not allow for a comprehensive quantitative comparison of the results. Other works on synergistic effects for the H-C reaction probability include those of Vietzke et al [3, 4] for keV Ar^+ and sub-eV H^0 atoms, and Yamada and Sone [5] for H^+ and sub-eV H^0. The possible presence of synergistic effects for carbon erosion of a graphite probe cap was also noted for a series of PLT discharges [6].

The object of this communication is to present and to compare new results on synergistic methane production due to combined H^+ and H^0 fluxes, obtained independently in our laboratories in Toronto and Jülich. Pyrolytic graphite samples from the same batch (obtained from Union Carbide) were used and the impacting particle fluxes and energies were selected to provide an overlap.

2. EXPERIMENT

While both sets of experiments, at Jülich and Toronto, were performed in UHV systems, using samples from the same batch, the actual experimental facilities (e.g., H^+ ion and H^0 atom sources) and procedures (e.g., methane detection technique) employed were different, and are described separately below.

2.1 Toronto Experiment

All experiments were performed in our UHV-Accelerator Facility; for details see Ref. [2]. The pyrolytic graphite sample (45 mm × 8.5 mm × 0.25 mm) was positioned at 45° to a beam of mass-analyzed H^+ ions, resulting in a beam spot of ~0.2 cm^2. Sample temperature variation was achieved by resistive heating and optical pyrometry was used for temperature monitoring. Prior to the methane production experiments the sample was baked at 2200K for about 4 minutes in order to reduce the inherent hydrogen

content. The H^+ ion beam intensity was normally measured on the sample, with the sample biased at ~20V to suppress secondary electrons; these meaurements were confirmed with a Faraday cup for some cases. Both H^+ and H_3^+ ions were used for the experiments, and from the results it is evident that the H_3^+ molecular ion behaves effectively as three H^+ ions, with one-third of the H_3^+ ion energy, vis a vis the methane formation process.

The sub-eV H^0 atoms were produced by contact dissociation of hydrogen molecules on a hot tungsten filament (~1900K), with the vacuum chamber backfilled with H_2. The W filament was parallel with the sample, and was about 5 mm in front of it. For in-situ measurement technique of H^0 flux density see, for example, Haasz et al [7].

The methane produced during the hydrogen-carbon interaction was monitored in the residual gas via the mass 15 signal with an Extranuclear quadrupole mass spectrometer, the sensitivity of which was calibrated using a known CH_4 leak. The quadrupole chamber was differentially pumped and was kept at a constant total pressure in order to maintain a consistent conditioning of the quadrupole, and thereby a constant sensitivity to CH_4.

2.2 Jülich Experiments

The experiments were performed in our plasma-wall-interaction apparatus described in previous papers [1]. The sub-eV H^0 atoms were produced by dissociation of H_2 in a resistively heated tungsten tube (2800K) positioned in a separately pumped UHV chamber. The atoms effusing through a small orifice, and passing through an aperture, formed a beam of ~3 mm diameter at the sample position. Beam intensities were evaluated from measurements of the hydrogen flow, the W tube temperature, and literature values of the H_2 dissociation rate. A cosine angular distribution of the effusing beam was assumed. The same area of the sample was bombarded simultaneously with the sub-eV H^0 atoms and hydrogen ions (1 keV - 2.5 keV energy) produced by a conventional ion gun.

The graphite samples were heated resistively and baked routinely at ~2200K prior to and between the experiments. The total gas pressure in the reaction chamber was about 10^{-7} Torr during the experiments. Reaction products resulting from the hydrogenic impact on graphite were directly detected by a two stage differentially pumped quadrupole mass spectrometer positioned perpendicular to the H^0 beam. This detection technique is described elsewhere [1].

For the evaluation of reaction yields, a Maxwell-Boltzmann velocity distribution corresponding to the target temperature was assumed. The sensitivity of the mass-spectrometer and the cracking pattern of various hydrocarbon gases were determined by a Knudsen-cell with known flow rates, directed towards the target position. Target temperatures were measured with an optical pyrometer. All Jülich experiments were performed at 800K graphite temperature.

3. DISCUSSION

3.1 Temperature Profiles

The Toronto experiments were performed for two H^+ ion energies (300 eV/H^+ and 1 keV/H^+) and for H^+ fluxes of 6×10^{12}-5×10^{15} H^+/cm^2s. For each energy-flux combination methane temperature profiles (i.e., methane production as a function of graphite temperature) were obtained for: (i) sub-eV H^0 impact only, (ii) H^+ ion impact only, and (iii) simultaneous impact by suv-eV H^0 atoms and H^+ ions, see Fig. 1. For most of the experiments steady-state methane production was attained at each temperature setting. For some of the low flux cases, however, excessively long times were required for the establishment of steady state conditions, and in cases where such conditions were not reached, hystereses were observed in the temperature profiles. Hystereses were also observed for H^+-only ion impact on graphite [8].

Over the flux range used for the synergistic bombardment experiments, only a small shift was observed in the temperature for maximum yield. For almost all experiments, the synergistic T_m fell between 775 and 800K, while for similar fluxes in the case of H^+-only bombardment, the T_m shifted from 725 to 800K [8]. The different behaviour could be attributed to the differences in total hydrogenic fluxes in the two cases. In the synergistic case the total flux to the surface is dominated by the H^0 flux, which was kept constant for these experiments.

Changing the H^+ ion energy from 300 eV to 1 keV/H^+ did not result in an appreciable change in the temperature profiles for the synergistic results; similar results were obtained for the H^+ ion-only cases [8,9]. However, when the ion energy is reduced to ~100 eV/H^+, noticeable broadening occurs for both synergistic [2] and ion-only bombardment [8,9].

3.2 Methane Formation Synergism

For the assessment of the synergistic effect, we introduce four different expressions with an attempt to highlight the significance of the results for tokamak aplications as well as to provide some insight into the mechanisms causing the effect.

(a) Synergistic Factor: $\xi \equiv [CH_4]_s / \{[CH_4]_{H^+} + [CH_4]_{H^0}\}$

The bracketed CH_4 terms denote the methane production rate (CH_4/cm^2s) and the subscripts s, H^+ and H^0 represent synergistic, H^+ ions-only and H^0 atoms-only cases, respectively. For graphite temperatures of 750 and 800K, the synergistic factor, as a function of ion to atom flux density ratio reaches a maximum value of about 10-15, corresponding to $[H^+]/[H^0] \sim 0.02$, see Fig. 2(a). While the experimental flux ratio is limited to a span of about three orders of magnitude, evidence of the expected trends for the limiting cases is apparent, viz, $\xi \to 1$ for $[H^+]/[H^0] \gg 1$ (ion dominated case) and $[H^+]/[H^0] \ll 1$ (atom dominated case). For the case of equal H^0 and H^+ fluxes, ξ being approximately equal to two implies that the increased methane formation due to the H^0 atoms is about the same as that due to the ions (note that for equal fluxes, under separate bombardment, $[CH_4]_{H^0} \ll [CH_4]_{H^+}$, see Fig. 1).

(b) Synergistic Yield: $Y_s = [CH_4]_s / \{[H^+] + [H^0]\}$

A plot of the synergistic-methane formation rate, $[CH_4]_s$, normalized by the total available hydrogenic flux, as a function of $[H^+]/[H^0]$, tends to the H^0 atoms-only case for $[H^+]/[H^0] \ll 1$, and the H^+ ions-only case for $[H^+]/[H^0] \gg 1$, see Fig. 2(b). As the flux ratio increases, the methane formation per incident hydrogen also increases, reaching a level of $Y_s \sim 0.08$ for equal H^0 and H^+ fluxes. Since this methane yield is also characteristic of the H^+ ions-only case for similar H^+ energies, flux densities and graphite temperature [8], the data in Fig. 2(b) imply that for equal fluxes of H^0 and H^+ the methane formation per incident H^0 atom is similar to that due to H^+ ions, as was noted from Fig. 2(a) above.

(c) $[CH_4]_s/[H^+]$

For tokamak applications, where H^+ fluxes are known quite accurately and only the order of magnitude of H^0 fluxes are available, a useful indicator for the synergistic effect is the synergistic methane formation rate to H^+-ion flux ratio. Since the H^0 flux is not included in the denominator, values of $[CH_4]_s/[H^+]$ do exceed Y_s, as seen in Fig. 2(c).

(d) Synergistic Enhancement Yield, $[CH_4]_\Delta/[H^0] = \{[CH_4]_S - [CH_4]_{H^+}\}/[H^0]$

A plot of $[CH_4]_\Delta/[H^0]$, as a function of $[H^+]/[H^0]$, indicates the enhanced methane formation per incident H^0 atom in the presence of H^+ ions, see Fig. 3(d). In the limiting case of no H^+ ions (i.e., $[H^+]/[H^0] = 0$) the enhancement yield reduces to the H^0 atoms-only case. For increasing $[H^+]/[H^0]$ flux ratios, the enhancement yield increases, reaching a level of ~0.08 for equal H^+ and H^0 fluxes, leading to the same conclusion as noted above. For higher ion fluxes, the enhancement yield rises above the H^+ ion-only yield, to a level ~0.1; this is very likely due to uncertainties in the H^0 flux density measurements.

3.3 Comparison of Toronto and Jülich Results

The reaction products detected by the direct line of sight technique in Jülich were mainly CH_3 with a smaller fraction of CH_4. The sum of these two products were used to evaluate the total methane formation yield. In the Toronto experiments where the methane was monitored in the residual gas, i.e., CH_3 and CH_4 could not be distinguished, the measured methane signal automatically includes the sum of CH_3 and CH_4. We therefore use the expression "methane formation" and also the abbreviation $[CH_4]$ to represent the formation of CH_3 plus CH_4.

The synergistic yield of methane formation obtained at Jülich and Toronto are in generally good agreement for values of $[H^+]/[H^0] < 0.1$ [see Fig. 2(b)]. Deviations of more than a factor of two, however, are observed for $[H^+]/[H] > 0.1$. The general trend of the Jülich result is a somewhat smaller asymptotic value for higher $[H^+]/[H^0]$. Since the Jülich results depend on the reaction product velocities through the quadrupole ionizer, velocities larger than the assumed Maxwellian distribution would tend to shift the Y_S curve to higher values, and closer to the Toronto curve. The observed differences between the two sets of results will, at least partially, be due to uncertainties in the determination of the different fluxes, especially the H^0 fluxes.

3.4 Reaction Spectrum by Simultaneous H^0 and H^+ Impact on Graphite

With the Jülich experimental set-up a detailed analysis of the formed reaction products in the simultaneous reaction of H^0 and H^+ with crbon has been performed for the H^+/H^0 flux ratio of 0.023, see Fig. 3. Consistent with previous results [1, 3] the main reaction channel is again the radical CH_3, whereby the CH_4 formation observed for the ions-only case is not

influenced significantly. In addition, significant production of C_2H_x and C_3H_x type hydrocarbons occurs. A reasonable fit of the measured ion signals within these groups is obtained by assuming the production of C_2H_2, C_2H_3, C_2H_4, C_2H_6, C_3H_6 and C_3H_8 as indicated in Fig. 3. Based on the sum of all hydrocarbon yields, the total carbon erosion is estimated to be ~3.5 times the methane formation yield for the H^+/H^0 flux ratio of 0.023 used here. The heavier hydrocarbon formation rates measured here are higher than those obtained by Yamada for H^+ irradiation alone [10]. However, preliminary new results show that the extent of the C_2H_x and C_3H_x formation depends on the H^+/H^0 flux ratio and H^+ energy, and therefore, the estimated factor of 3.5 cannot be used for all H^+/H^0 flux ratios.

4. CONCLUSIONS

Synergistic factors, indicating the extent of the methane enhancement for combined fluxes of H^+ and H^0 over individual species exposure cases, ranged from about 1.5 to 15. Present results are also in agreement with previously reported findings [1, 2]. For first-wall carbon tiles in tokamaks, where comparable Franck-Condon atom and energetic H^+ ion fluxes (or charge exchange neutrals) of the order 10^{15}-10^{16}/cm^{2}s are expected, the synergistic effect could lead to methane formation rates being at least twice the amounts based on H^+ fluxes alone. Should the $[H^+]/[H^0]$ flux ratio be lower, say about 0.1, then the methane production could be as much as an order of magnitude higher than the value based on H^+ ions alone; such conditions might occur at divertors. For the total chemical erosion by combined H^+ and H^0 irradiation the formation of heavier hydrocarbons will also have to be taken into account. Projection of the present data to limiters, where hydrogenic flux densities of ~10^{18}-10^{19}/cm^{2}s are expected, is somewhat uncertain due to the possible existence of saturation effects for the near-surface ion-induced damage and hydrogen concentrations.

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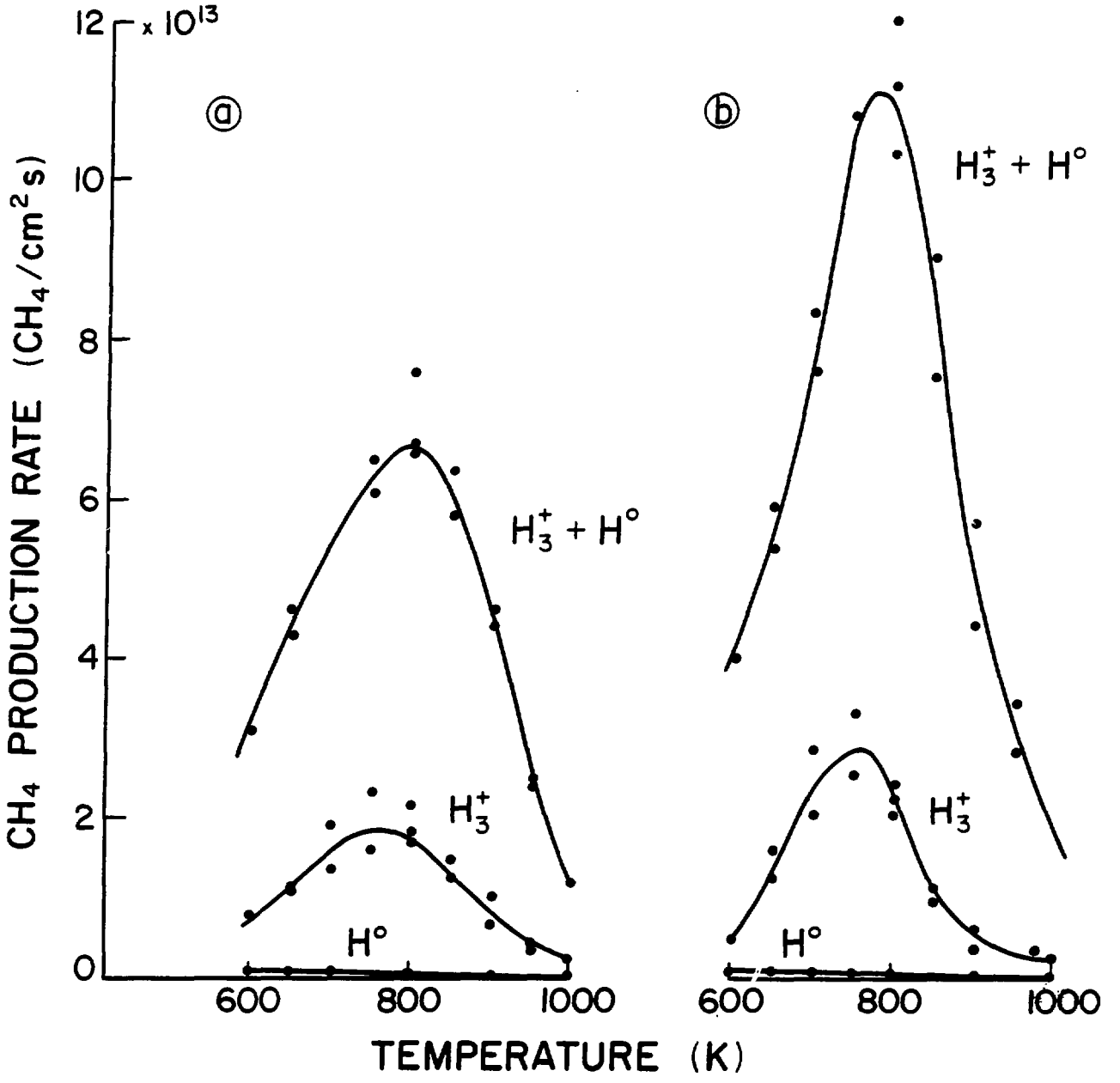

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FIGURE 1

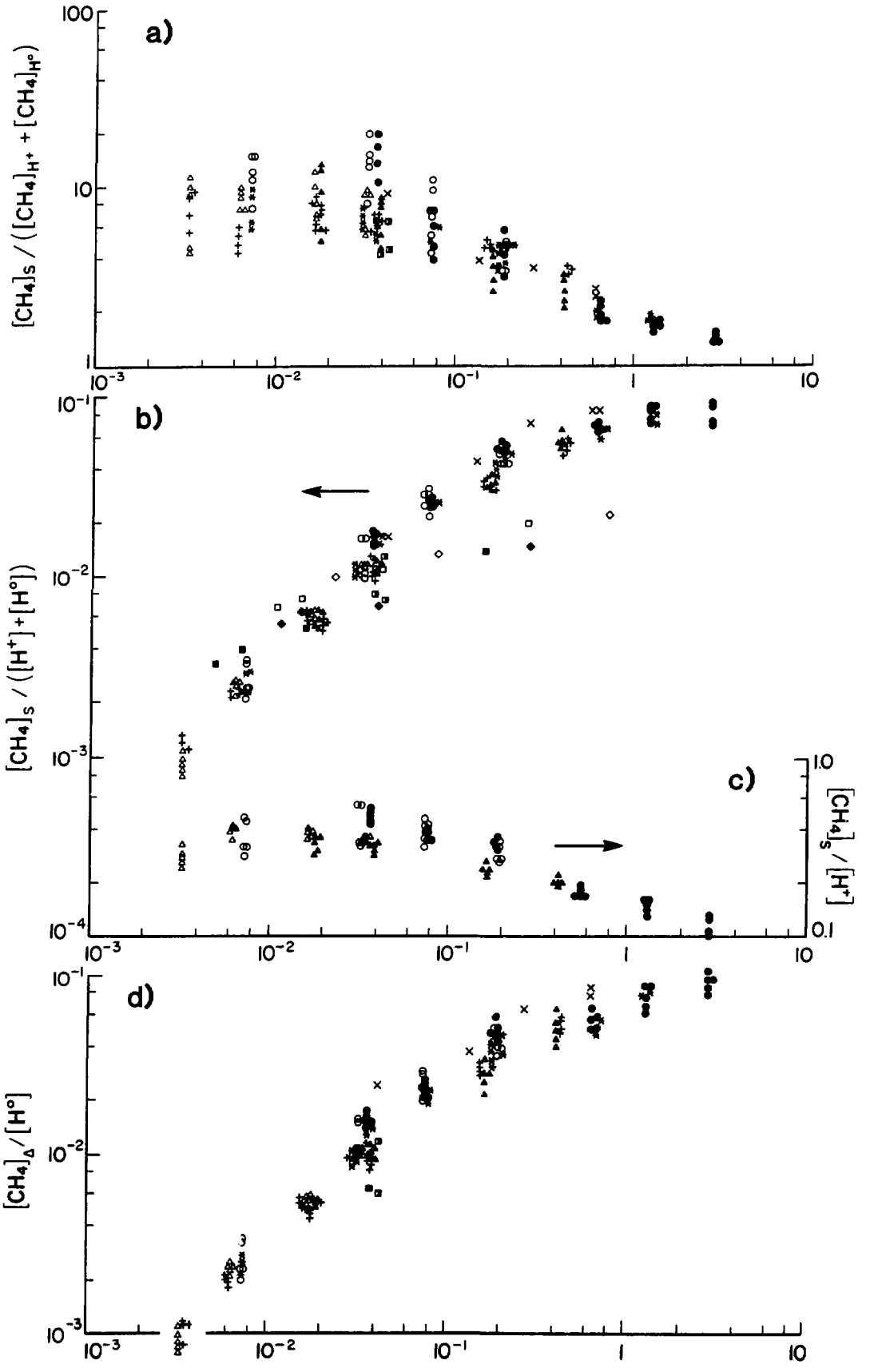

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FIGURE 2

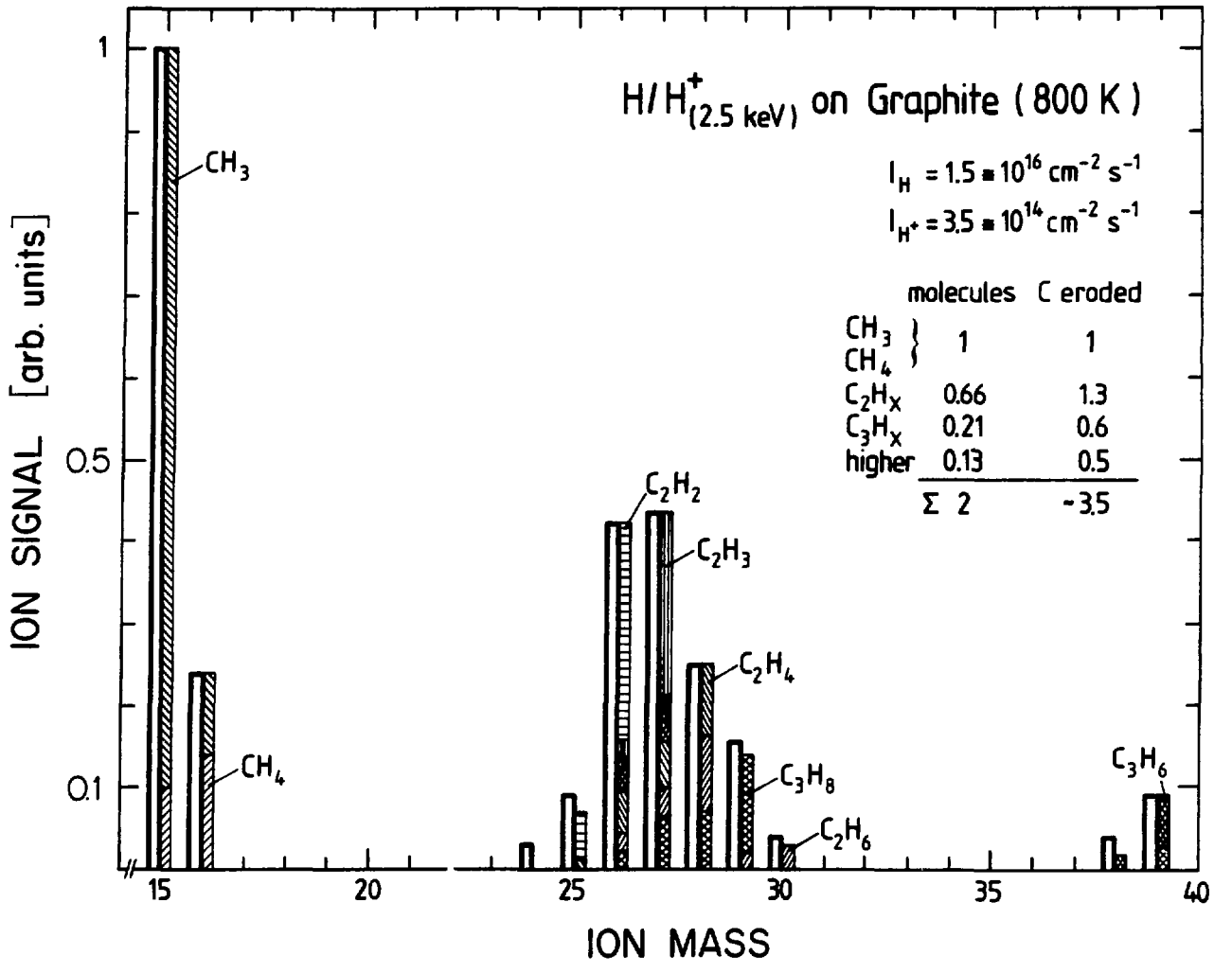

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FIGURE 3