Charge-transfer reactions of ground-state $C^+(^2P)$ and metastable-state $C^+(^4P)$ ions with H_2 molecules

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Cross sections for charge-transfer reactions of ground-state $C^+(^2P)$ and metastable-state $C^+(^4P)$ ions with H_2 have been measured in the 10- to 500-eV kinetic energy range. Ground-state reaction cross sections range from 0.3 to 0.5×10^{-16} cm^2, and the corresponding values for metastable state $C^+(^4P)$ ions vary from 20 to 12×10^{-16} cm^2. Both sets of cross-section values smoothly extrapolate to previously measured data at higher energies.

I. INTRODUCTION

In a tokamak fusion device the charge-transfer neutralization of impurity ions in the cold fuel at the device edge may contribute significantly to the production of slow hydrogen ions, which in turn leads to cooling of the plasma. The purpose of the present work is to establish the cross sections for neutralization of C^+, a common impurity, on H_2, the fuel, at energies up to a few hundred eV, which are typical of a tokamak-device sheath potential. It is well known that C^+ ions produced by dissociation of molecules may include a significant fraction in the metastable excited state and that the metastable-state cross section may be an order of magnitude greater than the ground-state cross section. Thus we seek to measure separately the cross sections for these two states.

The processes of interest are the neutralization of the ground-state ion

$$C^+(^2P)+H_2\rightarrow C^0+H_2^+ , \quad (1)$$

and of the metastable-state ion

$$C^+(^4P)+H_2\rightarrow C^0+H_2^+ . \quad (2)$$

The experimental technique measures the cross section for neutralization of C^+ and provides no information on the postcollision state of the H_2^+. If the H_2^+ is left in the ground state, then process (1) is endothermic by 4.16 eV while process (2) is exothermic by 1.18 eV. For process (2), if the H_2^+ ion is left in the $v=5$ vibrationally excited state, then the energy defect is almost zero.

The ion beam used in this experiment, and in much of the previously published work on charge-transfer neutralization of C^+, is produced by electron-impact dissociation of CO. Early experiments of Lindholm and coworker[1,2] have shown the C^+ ions, produced by electron-impact ionization of CO, are formed in both the ground ^2P state and the excited ^4P state. These workers[1,2] employed a tandem mass spectrometric apparatus in which ionic products from target molecule decompositions have been monitored after keV collisions with mass-analyzed C^+-ion beams. The features of this product ion spectra led these investigators to the conclusion that the abundances of $C^+(^2P)$ and $C^+(^4P)$ state ions initially formed in the electron-impact process were approximately 0.6 and 0.4, respectively. Lao, Rozett, and Koski[3] used a beam attenuation technique to measure relative abundances of 0.68 and 0.32 for $C^+(^2P)$ and $C^+(^4P)$ ions. However, it was found[4] that the $C^+(^4P)$ metastable-state abundance is a function of the ion source configuration as well as CO pressure in the ion source.[4–6] Jones *et al.*[7] used a reaction-ion-source–acceleration–quadrupole-mass-selector system and conditions similar to our instrumentation and they[7] found that 6% of the mass analyzed reactant C^+-ion beam was in the metastable state $C^+(^4P)$: a result identical to that obtained in this investigation.

II. EXPERIMENT

A schematic diagram of our experimental apparatus is shown in Fig. 1. The reactant C^+ ions have been formed by 100-eV electron-impact ionization of high-purity CO in a Nier-type[8] ion source. The ionizing electrons have been emitted from a directly heated tungsten filament, collimated into a beam, and accelerated into the source where ionization occurs. The ionizing electron beam current has been stabilized using an electron-trap-current–filament-current feedback circuit control supply. The energy of ionizing electrons has been determined by applied voltages and checked by measurement of the known Ar and CO ionization potentials. Care has been taken to physically shield the filament and ion source to prevent stray electrons and/or ions from reaching the acceleration region. In order to repel ions out of the electron beam in the ion source region, a small voltage has been applied to the ion repeller electrode. Ions gently repelled out of the source region have been collimated, slightly accelerated (<50 eV) and focused on the entrance aperture of a quadrupole mass filter. Mass-analyzed C^+ ions emerging from the mass filter have been focused by a quadrupole lens system and accelerated to terminal velocities by voltages applied to plates with circular openings. This C^+ ion beam has interacted with target gas H_2 in a collision chamber where C^+ charge-transfer reactions occur. Fine control needle valves have been used to allow high-purity gases into the respective ion source and collision chamber. Target-gas pressures in

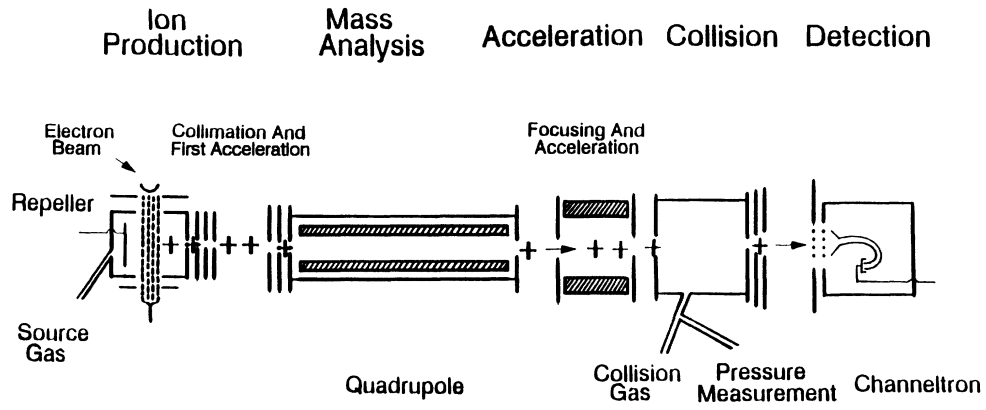

FIG. 1. Schematic diagram of collision apparatus used to study metastable enhancement of C^+ capture reactions.

the cylindrical collision chamber have been determined by a MKS Baratron pressure gauge. Ions exiting from the collision chamber proceed to the detection region where they are postaccelerated to approximately 3 keV and detected using a Bendix channeltron electron multiplier. The channeltron output has been measured using both a counting (Ortec) and current amplification (Keithly picoammeter) techniques. The detector has been shielded in a separate container to prevent stray photons and/or ions from reaching the channeltron. The entire apparatus has been contained in a stainless-steel vacuum chamber which has been evacuated by a 6-in., 3000 liter/sec diffusion pump and 500 liter/min mechanical roughing pump. Background pressures in the vacuum chamber were approximately 6×10^{-7} Torr.

III. RESULTS AND DISCUSSION

When an ion beam passes through a target gas in a collision chamber, the beam is attenuated exponentially as a function of gas concentration. The cross section for ion loss σ, which is dominated by electron transfer in our system, can be estimated from the ion beam flux I_0 determined without collision gas and the flux I at a given gas concentration by the use of the relation

$$I/I_0=\exp(-nl\sigma)\ , \tag{3}$$

where n is the number density of the target gas and l is the effective length of the collision chamber. A plot of $\ln(I/I_0)$ versus n should be linear with slope $l\sigma$, from which σ can be determined. Since the (100 eV) energy of electrons in our ion source is much larger than the 27.7-eV threshold of the long-lived excited-state $C^+(^4P)$ ions from CO, our reactant ion beam is expected to contain metastable states. Higher excited states may also be present initially, but will decay radiatively before entering the target region. A mixed-state ion beam (with ground-state fraction f_g and metastable-state fraction f_m) follows the attenuation relation

$$I/I_0=[f_g\exp(-nl\sigma_g)+f_m\exp(-nl\sigma_m)]\ , \tag{4}$$

where $f_m=1-f_g$ and σ_g and σ_m refer to cross sections for ground and metastable states, respectively. In the case where the cross sections for reactions of ground- and metastable-state ions are significantly different, it is possible to resolve the curve of $\ln(I/I_0)$ verses n into two components, one from reactions of ground-state $C^+(^2P)$ ions and another from reactions of ground- and metastable-state ions. One of our typical attenuation curves for charge transfer reactions of mixed-state C^+ ions with H_2 is shown in Fig. 2 and illustrates error estimates. Cross sections for metastable-state $C^+(^4P)+H_2$ reactions are an order of magnitude larger than the corresponding ground-state $C^+(^2P)+H_2$ cross sections. The values of I/I_0 drop very rapidly at low target-gas concentration due to the exponential $(-nl\sigma_m)$ term and as a result the $\ln(I/I_0)$ values at high (nl) are due only to ground-state $C^+(^2P)$ reactions. The slope of the $\ln(I/I_0)$ curve at large (nl) is essentially governed by σ_g. Extrapolation of this curve to zero target-gas concentration yields an intercept equal to $\ln f_g$. Given the values of f_g, σ_g, and nl, the σ_m has been deduced by fitting Eq. (4) to

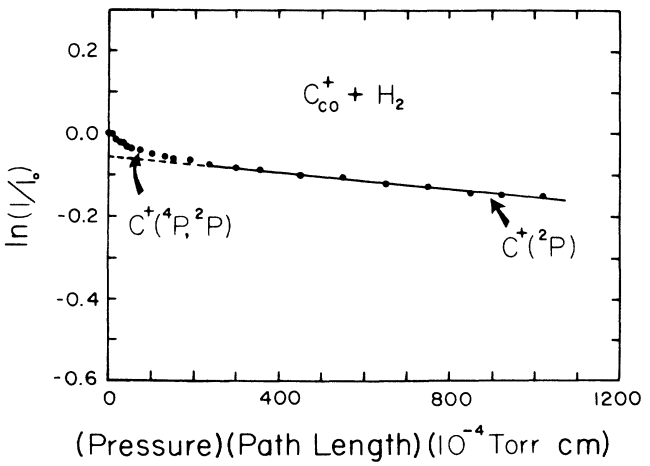

FIG. 2. Attenuation curve for mixed-state C^+ ion beam as a function of H_2 target-gas pressure times path length.

experimental I/I_0 values at low target-gas concentrations.

The data of Fig. 2 are for an ion beam produced by 100-eV electron impact on CO in a source at a pressure of about 10^{-1} Torr. Analysis of Fig. 2 shows that 6% of the beam was metastable ions, a fraction identical to that quoted by Jones *et al.*,[7] for a similar situation. For lower source pressures one observes higher metastable fractions as noted previously.[4-6]

Analysis of data such as Fig. 2 gives directly the ratio of metastable- and ground-state cross sections from the ratio of the exponents of the two decay curves. Moreover, the slopes of the curves, in arbitrary units, can be used to establish the relative variation of cross section with projectile energy. Both the ratios of cross sections, and the relative variation of cross section with projectile energy are obtained directly without a need for calibration. To place the data on an absolute basis we must determine the absolute value of *nl*, target density times cell length. Two approaches were used. The first method was to calculate *nl* directly with corrections for pressure drops in the tubing between manometer and cell as well as corrections for nonuniformity of target-gas density close to the ion beam entrance and exit apertures; for this we used the prescriptions of Van Zyl, Chamberlain, and Dunn.[9] The second approach was to study the attenuation of $C^+(^2P)$ in N_2 at 100 eV, for which a cross section is known from previous publications,[3] and use this to estimate an effective value of *nl*. The two approaches agree within 7%, which is well within the combined limits of reliability. We have some concern about the validity of approximations used in the calculation method and have therefore chosen rather to use the values determined experimentally on the basis of previously published data.[3]

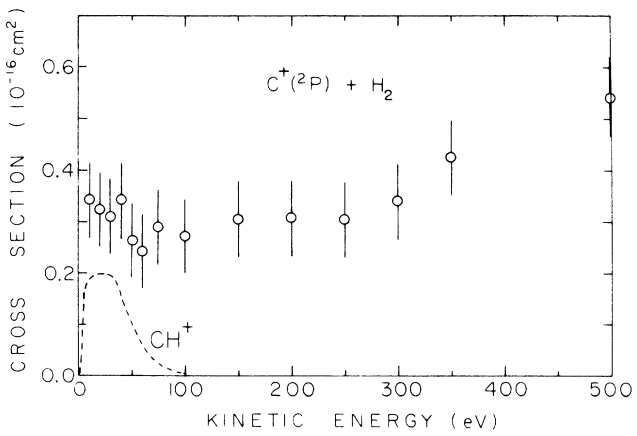

FIG. 3. Charge-transfer cross sections (10^{-16} cm^2) as a function of reactant ion kinetic energy (eV) in $C^+(^2P)+H_2$ reactions. The open circles represent the cross sections obtained in this investigation while the dashed line gives the cross sections measured for the rearrangement channel $C^+(^2P)+H_2 \rightarrow CH^+ + H$ by Ervin and Armentrout (Ref. 11), which have been multiplied by 0.1 for display purposes. The present cross sections below 75 eV may refer to a composite of charge-transfer and rearrangement reactions.

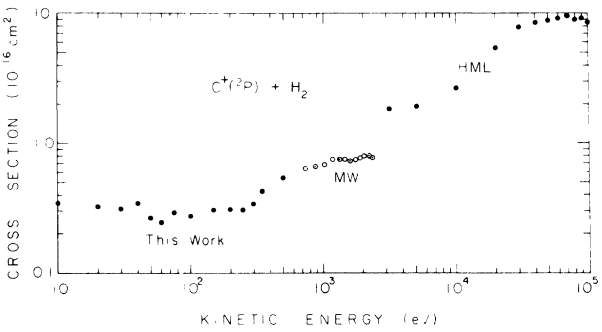

FIG. 4. Charge-transfer cross sections (10^{-16} cm^2) as a function of reactant kinetic energy (eV) in $C^+(^2P)+H_2$ reactions. Closed circles at low ion kinetic energies are the cross sections measured in this investigation. The open circles labeled MW represent data of Ref. 10 while the closed circles at high energies labeled HML represent data of Ref. 13. The present cross sections below 75 eV may refer to a composite of charge-transfer and rearrangement reactions.

Thus the absolute value of cross sections displayed here should be regarded as being established by normalization to the previous data on neutralization of $C^+(^2P)$ in N_2 by Lao, Rozett, and Koski,[3] which are also consistent with the work of Moran and Wilcox.[10] The data of Lao, Rozett, and Koski[3] are a particularly appropriate case for comparison since the C^+ ions were produced by ionization of CO at 23-eV electron energies where only $C^+(^2P)$ ions can result and the data are not complicated by participation of excited-state ions. The reliability of absolute magnitude is entirely dependent on the value of *nl*. We estimate this to be ±7%, the limit of agreement between the two techniques used for its determination.

Ground-state cross sections measured in this investigation are displayed as open circles in Fig. 3 and cover the kinetic energy range of 10–500 eV. The error bars denote the reproducibility of our experimental attenuation cross sections and range from ±12 to ±23 % depending on ion kinetic energy. We should note that data below 75 eV may be in error due to the influence of the reaction $C^+(^2P)+H_2 \rightarrow CH^+ + H$ where large angular scattering may occur; for reference the measurements by Ervin and Armentrout[11] on total CH^+ formation are also shown, multiplied by 0.1 for convenience. A fraction of the CH^+ ions can be scattered into large angles[7,12] and therefore contribute to attenuation; although no attenuation term attributable to this reaction can be detected in our measurements, it cannot be completely ruled out. CH^+ formed with negligible angular scattering may be included in the transmitted C^+ count. Since there is no postcollision mass analysis, this component would not contribute to attenuation. Thus the data below 75 eV may refer to a composite of charge-transfer and rearrangement collisions and should be treated with caution. The data above 75 eV are considered to reliably represent the process described by Eq. (1).

The ground-state $C^+(^2P)+H_2$ cross sections obtained in this work are compared with charge-transfer cross sec-

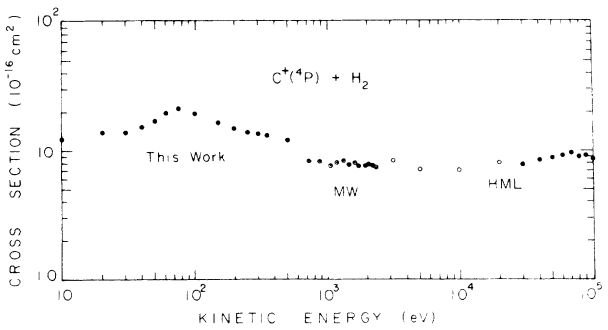

FIG. 5. Charge-transfer cross sections (10^{-16} cm^2) as a function of reactant kinetic energy (eV) in $C^+(^4P)+H_2$ reactions. Closed circles at low ion kinetic energies are the cross sections measured in this investigation. The ⊙ circles labeled MW represent data of Ref. 10 while the closed circles labeled HML represent data of Ref. 13. The open circles from 3 to 20 keV are data of Ref. 13 with f_m taken as 0.32.

tions obtained by other investigators in Fig. 4. The closed circles representing ion beam attenuation data of this work at low ion kinetic energies smoothly join to ground-state $C^+(^2P)$ charge-transfer cross sections measured in Ref. 10 at higher (0.7–3.0 keV) kinetic energies. Time-of-flight techniques were used by Ref. 10 to monitor fast C neutrals produced in $C^+(^2P)+H_2$ charge-transfer collisions. The cross sections measured by Hoffman, Miller, and Lockwood over the 3–100-keV energy range were obtained by detection of the fast neutrals from a magnetically selected ground-state C^+ ion beam.[13] Although the three different sets of ground-state cross-section data were obtained using various experimental arrangements at different ion kinetic energies, the trend in the charge-transfer cross sections as a function of ion kinetic energy is clear. Cross sections approximating 0.3×10^{-16} cm^2 at eV energies tend to gradually increase with ion energy to a maximum around 10×10^{-16} cm^2 at 70 keV and then to decrease at higher energies.

The cross sections for the charge-transfer reaction $C^+(^4P)+H_2$ have been determined from application of Eq. (4) to attenuation data at low target-gas pressures. The cross sections for $C^+(^4P)$ excited-state reaction are more than an order of magnitude larger than those involving $C^+(^2P)$ ground-state ions. The $C^+(^4P)$ cross sections are displayed in Fig. 5 as closed circles from 10 to 500 eV along with data from other investigations of this excited-state reaction. The open circles in the 0.7–2.4-keV range refer to the excited-state reactions of Ref. 10 in which fast neutral products were detected. The closed circles illustrate the 30–100-keV data of Ref. 13 while the open circles from 3 to 20 keV are estimated from the data of Ref. 13 assuming $f_m=0.32$.

The data in Fig. 4 and 5, from the present work at energies ≤ 500 eV and previous work at higher energies, are from three entirely different experimental techniques where the influence of metastable species has been properly assessed. The three data sets extrapolate smoothly from one energy range to the next over a range from 10 to 10^4 eV. At energies above 20×10^3 eV the cross sections for ground and metastable species are the same at about 10 Å^2. As energy decreases from 20×10^3 to 10 eV, the metastable-state cross section remains approximately constant while the ground-state cross section falls by a factor of 30.

Not shown in Fig. 4 are data by Phaneuf, Meyer, and McKnight[14] and by Nutt, McCullough, and Gilbody,[15] which purport to represent neutralization of ground state C^+. The work of Phaneuf, Meyer, and McKnight[14] involved no attempt to identify the metastable content of their ion beam. The data, which are for energies above 8.6 keV, are in good agreement with the ground-state data of Hoffman, Miller, and Lockwood.[13] The work of Nutt, McCullough, and Gilbody[15] extends from 0.2 to 13 keV, overlaps all three data sets on Figs. 4 and 5, lies between the metastable- and ground-state cross sections, and does not exhibit the energy dependence of either. Nutt, McCullough, and Gilbody[15] used in electron impact source, as did the authors of all work shown in Figs. 4 and 5; they attempted to detect metastable states by the same attenuation technique as we used, here but claimed no metastable states were detectable. Interestingly the data of Nutt, McCullough, and Gilbody[15] are in reasonable agreement with Moran and Wilcox's[10] total cross section for a mixed metastable- and ground-state beam where the metastable-state fraction was 0.32. We have used the three data sets of Figs. 4 and 5 to predict a total cross section for attenuation of a C^+ beam that is composed of 68% neutral species and 32% metastable states. The data of the present work, the work of Moran and Wilcox[10] and that of Hoffman, Miller, and Lockwood,[13] illustrated in Fig. 6, all predict a total attenuation cross section for this mixed beam which agrees adequately with the work of Nutt, McCullough, and Gilbody;[15] the disagreements are of the order 30% or less, which is within the error limits of the data sets. One might conclude that the data of Figs. 4 and 5 are consistent with

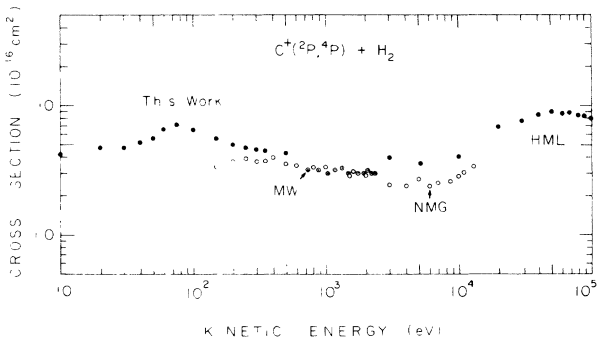

FIG. 6. Charge-transfer cross sections (10^{-16} cm^2) as a function of reactant kinetic energy (eV) in mixed-state beam $C^+(^2P,^4P)+H_2$ reactions. Closed circles at low ion kinetic energies are the cross sections measured in this investigation with $f_m=0.32$. The ⊙ circles are the mixed beam data of Ref. 10 and the closed circles at high energies are the mixed beam data of Ref. 13. The open circles are the cross sections measured in Ref. 15.

the work of Nutt, McCullough, and Gilbody provided one assumes that the latter authors did in fact have a 32% metastable content in their ion beam.

The three experiments displayed in Figs. 4 and 5 use three entirely different experimental techniques. Nevertheless the cross-section data merge as one passes from one range to another. Our confidence in the general trend of the data sets is enhanced by the observation that all three are consistent also with the data of Nutt, McCullough, and Gilbody,[15] provided that we assume the latter involves a mixed beam with 32% metastable states.

Reaction cross sections are much larger for reactant C^+ ions in the metastable state ^4P than those in the ground state ^2P. The increased reactivity of the metastable-state $C^+(^4P)$ ions over that of the ground-state $C^+(^2P)$ ions can be rationalized considering the energetics of those two reactions. The recombination energy of $C^+(^2P)$ ions is only 11.27 eV and the electron-transfer reaction producing H_2^+ is 4.16 eV endothermic. As such, this reaction is not expected to occur with high probability at low reactant ion kinetic energies. However, there is reasonably close energy balance between the $C^+(^4P)$ 16.60-eV recombination energy and the energy required to form product H_2^+ in the fifth vibrational level with the result that much larger cross sections are expected for this near-resonant charge-transfer reaction.

ACKNOWLEDGMENTS

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