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Charge transfer reactions of ground $O^+(^4S)$ and metastable $O^+(^2D, ^2P)$ ions with H_2 molecules

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Abstract. Cross sections for charge transfer reactions of ground $O^+(^4S)$ and metastable $O^+(^2D, ^2P)$ state ions with H_2 have been measured for reactant ions with 10 to 500 eV kinetic energies. Ground-state ion cross sections range from 0.5 to 0.9×10^{-16} cm^2 and metastable-state ion cross sections are approximately constant at 10×10^{-16} cm^2.

1. Introduction

Charge transfer reactions of impurity ions, such as O^+, in cold H_2 fuel at the edge of a Tokamak fusion device can contribute greatly to the production of slow hydrogen ions which in turn lead to cooling of the plasma. The purpose of this investigation is to determine cross sections for charge transfer reactions between O^+, a common impurity, and H_2 fuel over the 10 to 500 eV kinetic energy range, which is appropriate for ions in a sheath potential of a Tokamak device. Many previous studies of charge transfer reactions have assumed that only ground-state ions contribute to formation of product species. However, ion beams produced by high-energy electron impact ionisation may include components of long-lived excited states and these states may significantly affect measured total cross sections. The present investigation will focus on determination of charge transfer cross sections of $O^+(^4S)$ as well as metastable $O^+(^2D, ^2P)$ state ions with H_2 in the reactions

$$O^+(^4S) + H_2(X\,^1\Sigma_g^+, v''=0) \rightarrow O + H_2^+ \tag{1}$$

$$O^+(^2D, ^2P) + H_2(X\,^1\Sigma_g^+, v''=0) \rightarrow O + H_2^+. \tag{2}$$

2. Evidence for both gound- and metastable-state O^+ ions

Electron impact ionisation of CO leads to production of O^+ ions. The threshold for formation (Rosenstock *et al* 1977) of ground state $O^+(^4S)$ and $C(^3P)$ in the reaction

$$e(24.7\text{ eV}) + CO(X\,^1\Sigma^+, v=0) \rightarrow O^+(^4S) + C(^3P) \tag{3}$$

is 24.7 eV. The minimum energy to produce metastable state $O^+(^2D)$ ions is 3.32 eV higher than that for forming ground-state $O^+(^4S)$ ions. The minimum energy required to form $O^+(^2P)$ ions is 5.02 eV higher than that of ground-state $O^+(^4S)$ ions (Moore

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1949). Higher-energy electron impact ionisation of CO has been shown (Lindholm 1966) to lead to formation of ground $O^+(^4S)$ as well as $O^+(^2D)$ and $O^+(^2P)$ state ions. The lifetimes (Defence Nuclear Agency 1972) of these O^+ excited states are $^2D^o_{3/2} = 5.9 \times 10^3$ s, $^2D^o_{5/2} = 2.1 \times 10^4$ s, $^2P^o_{1/2} = 5.4$ s and $^2P^o_{3/2} = 4.2$ s. As a result of these long lifetimes, the $O^+(^2D)$ and $O^+(^2P)$ state ions are metastable and available for ion–molecule reactions. Thermal energy drift-tube measurements of Johnsen and Biondi (1980) and the selected ion-flow-tube experiments of Glosik *et al* (1978) have measured rate constants for reactions of these metastable O^+ state ions. Early investigations (Lindholm 1966, Turner *et al* 1968, Hughes and Tiernan 1971) have shown a high relative abundance of metastable O^+ ions in a beam formed by energetic electron impact ionisation of a variety of precursor molecules. Evidence for metastable $O^+(^2D)$ and $O^+(^2P)$ state ions in the ionosphere has been summarised in the review article of Smith and Adams (1980). Translational spectroscopy experiments (Hamdan and Brenton 1988, 1989) have indicated that the long-lived ^2D and ^2P metastable states comprise a significant fraction of ions in an O^+ beam. Hamdan and Brenton (1989) determined the $O^+(^4S)$, $O^+(^2D)$ and $O^+(^2P)$ relative abundances to be 0.55, 0.25 and 0.20 respectively for 100 eV electron impact ionisation of O_2. Lindholm (1966) estimated the corresponding $O^+(^4S)$, $O^+(^2D)$, and $O^+(^2P)$ relative abundances to be approximately 0.3, 0.3 and 0.4 for O^+ ions produced by ionisation of CO. Lindholm (1966) arrived at these qualitative values by examination of product-ion fragmentation spectra observed in (O^+ + molecule) interactions in keV collisions. Selected ion-flow-tube measurements (Glosik *et al* 1978) of O^+, from ionisation of CO, have indicated that less than 10% of the O^+ ions occupy the ^2D and ^2P excited states. Nutt *et al* (1979) estimated the O^+ metastable fraction to be approximately 0.19 from an ion beam attenuation technique. The apparent discrepancies between O^+ metastable state abundances from ionisation of CO can be attributed to different ion source/acceleration/mass analysis configurations in the various systems (Lindholm 1966, Glosik *et al* 1978, Nutt *et al* 1979). It is well known that use of high-pressure ion sources (Sullivan-Wilson *et al* 1970, Leventhal 1971, Lindemann *et al* 1972) can lead to significant loss of metastable-state ions due to collisional quenching mechanisms. Indeed, Rowe *et al* (1980) observed loss of $O^+(^2D)$ and $O^+(^2P)$ state ions in the reaction

$$O^+(^2D, ^2P) + CO \rightarrow CO^+ + O \tag{4}$$

with a rate constant of 1.3×10^{-9} cm^3 s^{-1} which is four orders of magnitude larger than the corresponding ground-state $O^+(^4S) + CO$ reaction. The CO pressure in our ion source, on the order of 10^{-1} Torr, is expected to a result in partial depopulation of $O^+(^2D, ^2P)$ metastable states initially produced in electron impact ionisation and thus result in relatively low O^+ metastable ion abundances.

3. Experimental method

The experimental ion beam apparatus used in the investigation has been described previously (Xu *et al* 1990), however a brief outline of essential features is in order. Ionising electrons have been emitted from a directly heated tungsten filament, collimated into a beam, and accelerated into the ion source where interactions with neutral molecules occur. The ionising electron energy has been determined from applied voltages and confirmed by measurement of the known CO ionisation energy. Reactant

O^+ ions employed in this investigation have been produced by 100 eV electron bombardment of high purity CO. Ions are repelled out of the electron beam in the source region by a small voltage applied to an ion repeller electrode. Ions emerging from the source region have been collimated, slightly accelerated (<50 eV) and focused on the entrance aperture of a quadrupole mass filter. The mass-analysed O^+ ions exiting the quadrupole have been focused and accelerated to terminal velocities by voltages placed on a series of plates with circular apertures and a quadrupole lens system. This O^+ ion beam has interacted with target gas H_2 in a collision chamber where O^+ charge transfer reactions occur. The H_2 target gas pressures in the collision chamber have been monitored by a MKS Baratron pressure gauge. Unattenuated O^+ ions, which have not reacted, proceed from the collision chamber to detection region where they are postaccelerated to approximately 3 keV and detected using a Bendix channeltron electron multiplier. Electrons from the channeltron have been measured using both a counting (Ortec) and current amplification (Keithly picoammeter) techniques. The channeltron has been shielded in a separate container to prevent stray photons and/or ions from reaching the channeltron. This ion beam collision apparatus has been evacuated by a 6 in, 3000 l s^{-1} diffusion pump and 500 l min^{-1} mechanical roughing pump and background pressures in this vacuum chamber were approximately 6×10^{-7} Torr.

4. Results and discussion

Ion beam attenuation techniques have been used to advantage in experiments (Turner *et al* 1968, Lao *et al* 1968, Nutt *et al* 1979) which have attempted to determine charge transfer cross sections for reactant ion beams with a mixed state distribution. The attenuation method is particularly useful for change transfer reactions in which the cross sections involving ground- and excited-state ions differ significantly from one another. In this technique, an ion beam passing through a target gas in a collision chamber is attenuated exponentially as a function of gas concentration. Cross sections for ion loss σ can be determined from the ion beam flux I_0 without collision gas and the flux I at a given gas concentration with the aid of the relation

$$I/I_0 = \exp(-nl\sigma) \tag{5}$$

where n is the number density of the target gas molecules and l is the effective length of the collision chamber. A plot of $\ln(I/I_0)$ as a function of nl should be linear with slope σ. If the ion beam contains both ground- and metastable-state components with different cross sections σ_g and σ_m, then the attenuation relation is

$$I = I_0[f_g \exp(-nl\sigma_g) + f_m \exp(-nl\sigma_m)] \tag{6}$$

where f_g and f_m are the ground and metastable fractions respectively and $f_g + f_m = 1$. If the two cross sections are greatly different, then a plot of $\ln(I/I_0)$ can be resolved into two separate linear components from which σ_g and σ_m can be separately determined. In the present investigation, we employ 100 eV electron energies in our source so that the beam may contain ground state $O^+(^4S)$ as well as both metastable $O^+(^2D)$ and $O^+(^2P)$ species.

A typical attenuation curve for O^+ in H_2 is illustrated in figure 1. At high target gas densities, the plot is a straight line from which a cross section may be deduced.

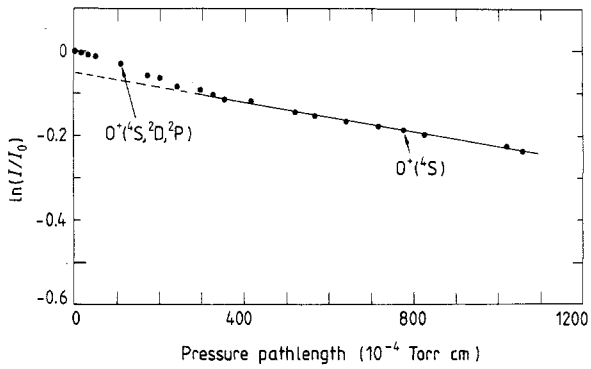

Figure 1. Attenuation curve for mixed-state O^+ ion beam as a function of H_2 target gas pressure.

At low target gas densities, there is a second component which is interpreted as being due to metastable ions in the beam and from which a cross section may be determined with the aid of equation (6).

The data of figure 1 are similar to those of Turner *et al* (1968) and Nutt *et al* (1979). Following these previous investigators, we interpret the attenuation at high densities as due to charge transfer neutralisation of the ground-state ion and the second component at low densities as due to neutralisation of the metastable-state ion. There are in fact two possible metastable states $O^+(^2D)$ and $O^+(^2P)$, although only a single component attributed to attenuation of metastables is observed in the present as well as the previous investigations. It seems likely that the two metastable states have approximately the same cross section, as has been shown recently for O^+ neutralisation in N_2 (Lavollée and Henri 1989), so that they contribute only a single attenuation component. Reaction energetic considerations supporting this conjecture are given later. We therefore interpret the data of figure 1 as giving a cross section for ground-state $O^+(^4S)$ ions and a cross section for an unresolved mixture of $O^+(^2D)$ and $O^+(^2P)$ metastable-state ions.

Extrapolation of the high-density component to zero pressure indicates that 95% of the ions arriving at the collision chamber are in the $O^+(^4S)$ ground state; this is for the case of 100 eV electron impact ionisation on CO in the ion source at a pressure of 10^{-1} Torr. The data of figure 1 show that 5% of our ion beam is in the metastable state(s) and that $\sigma_m > \sigma_g$.

Analysis of data such as those in figure 1 gives directly the ratio of metastable and ground state cross sections from the ratio of the exponents of the two (only) decay curves. Moreover, the slopes of the curves, in arbitrary units, can be used to establish the relative variations of cross sections with projectile energy. Both the ratios of cross sections, and the relative variations of cross sections with reactant ion energy, are obtained directly without a need for calibration. The data may be placed on an absolute basis by determining *nl*, the product of target density and collision cell length. This was determined first from pressure and cell length measurements with corrections for pressure gradients using the prescriptions given by Van Zyl *et al* (1976). Independently, we determined *nl* by studying $C^+(^2P)$ neutralisation in N_2 with the same apparatus and normalising our data to the 100 eV cross section published by Lao *et al* (1968). The two results agreed to within 7%. We have chosen to present the data as normalised

to the work of Lao *et al* (1968). The absolute accuracy is assessed at ±7%, the level of agreement between the two calibration techniques. Reproducibility of measurement was ±15%.

Ground-state cross sections obtained from attenuation data are presented in table 1. The $O^+(^4S)+H_2$ charge transfer cross sections are compared with those obtained by other investigators in figure 2. Full circles represent data of this investigation at low ion kinetic energies. The open circles are ground $O^+(^4S)$ state charge transfer cross sections measured by Moran and Wilcox (1978) at higher (0.6 to 3.0 keV) kinetic energies. Time-of-flight techniques were used in their experiments (Moran and Wilcox

Table 1. Cross sections (10^{-16} cm^2) for $O^+(^4S)+H_2$ ($X\,^1\Sigma_g^+$, $v''=0$) and O^+ (^2D, ^2P)$+H_2$ ($X\,^1\Sigma_g^+$, $v''=0$) charge transfer reactions.

Ion kinetic energy (eV)	$\sigma_g(O^+\,^4S)$ (10^{-16} cm^2)	$\sigma_m(O^+\,^2D, ^2P)$ (10^{-16} cm^2)
10	0.505	9.8
20	0.596	10.2
30	0.558	9.7
40	0.471	10.4
50	0.596	10.8
60	0.574	10.7
75	0.555	10.1
100	0.613	11.5
150	0.613	11.0
200	0.679	10.8
250	0.716	10.2
300	0.734	10.6
350	0.690	10.8
500	0.904	9.9

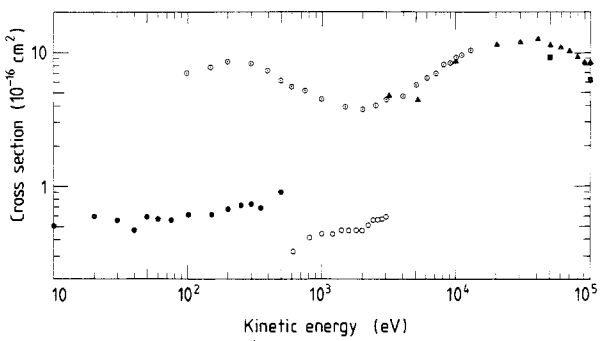

Figure 2. Charge transfer cross sections (10^{-16} cm^2) as a function of reactant kinetic energy (eV) in $O^+(^4S)+H_2$ reactions. Full circles at low ion kinetic energies are the cross sections measured in this investigation. The dotted open circles represent the data of Nutt *et al* (1979), the open circles represent data of Moran and Wilcox (1978), the triangles at high energies represent data of Hoffman *et al* (1982) while the squares at high energies represent data of Phaneuf *et al* (1978).

1978) to monitor fast O neutrals produced in O^+ (^4S) + H_2 charge transfer collisions. Attenuation cross sections of Nutt *et al* (1979), represented by dotted open circles in figure 2, disagree with the results of Moran and Wilcox (1978) and the present work in both magnitude and energy dependence. We offer no explanation for the apparent disagreement between the data of Nutt *et al* (1979) and the cross sections we have measured. The cross sections measured by Hoffman *et al* (1982), shown as triangles over the 3 to 100 keV energy range, were obtained by detection of the fast neutrals from a magnetically selected ground O^+ ion beam. The squares at 50 and 100 keV are data of Phaneuf *et al* (1978).

The cross sections of charge transfer reactions of metastable O^+ ions have been determined from application of equation (6) to attenuation at low target gas pressure and are given in table 1 as a function of ion kinetic energy. The cross sections for the metastable O^+ ions, in ^2D and ^2P states, are one order of magnitude larger than those involving $O^+(^4S)$ ground-state ions. The $O^+(^2D, ^2P)$ cross sections are displayed in figure 3 as full circles from 10 to 500 eV along with data from other investigations of these metastable state reactions. Open circles in the 0.6 to 3.0 keV range refer to metastable state reactions measured by Moran and Wilcox (1978) in which fast neutral products were detected. The triangles illustrate the 30–100 keV data of Hoffman *et al* (1982) while the squares represent the 50 and 100 keV data of Phaneuf *et al* (1978). Hoffman *et al* (1982) have demonstrated that the cross sections for metastable and ground state species are identical for kinetic energies above 20 keV. Thus we are justified in presenting the data of Hoffman *et al* (1982) in figure 3, over the 30 to 100 keV energy range, as well as the mixed-beam data of Phaneuf *et al* (1978) at 50 and 100 keV for comparison with our excited-state data.

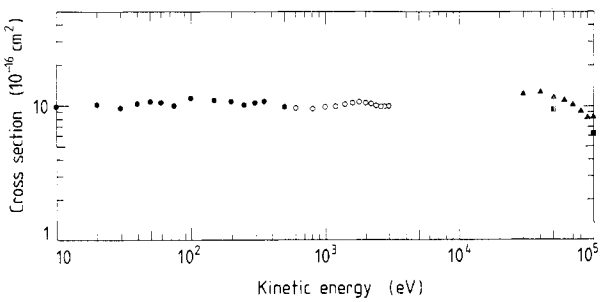

Figure 3. Charge transfer cross sections (10^{-16} cm^2) as a function of reactant kinetic energy (eV) in metastable $O^+(^2D, ^2P) + H_2$ reactions. Full circles at low ion kinetic energies are the cross sections measured in this investigation. The open circles represent data of Moran and Wilcox (1978), the triangles at high energies represent data of Hoffman *et al* (1982) while the squares at high energies represent data of Phaneuf *et al* (1978).

Gustafsson and Lindholm (1960) have also studied neutralisation of O^+ in H_2 using a mixed state O^+ beam, the composition of which was separately reported by Lindholm (1966). Their experiments were performed in the 50 to 900 eV energy range using O^+ ions produced from CO source gas. It was determined that the metastable fraction comprised 70% of the O^+ ion beam and these data are displayed as open squares in figure 4. Similar mixed-beam data of Hoffman *et al* (1982), Lockwood *et al* (1978) and Phaneuf *et al* (1978) covering the 3 to 100 keV energy range are given by triangles,

dotted open circles and full squares respectively. Using the present separate values of σ_g and σ_m, we have computed apparent cross sections σ_a from the relation

$$\sigma_a = f_g\sigma_g + f_m\sigma_m \tag{7}$$

with $f_m = 0.70$. These apparent cross sections calculated from data in figures 2 and 3 are displayed as full circles in figure 4 from 10 to 500 eV. The open circles in figure 4 spanning 0.6 to 3 keV represent σ_a computed from (7) using ground- and metastable-state cross sections of Moran and Wilcox (1978) with $f_m = 0.7$ in order that comparisons can be made with O^+ (from CO) mixed-beam data. Cross sections displayed in figure 4, from six separate investigations covering four orders of magnitude in energy, are in good agreement with one another and lend confidence to the present results.

The increased reactivity of the metastable state $O^+(^2D, ^2P)$ ions over that of the ground state $O^+(^4S)$ ions in this work can be rationalised by consideration of the energetics of charge transfer product channels which are in nearest energy resonance with reactants. The recombination energies for the following neutralisation processes $O^+(^4S) \rightarrow O(^3P)$, $O^+(^2D) \rightarrow O(^3P)$ and $O^+(^2P) \rightarrow O(^1D)$ are 13.618 12 eV, 16.941 97 eV and 16.66806 eV respectively (Moore 1949). The respective $H_2(X\,^1\Sigma_g^+, v''=0) \rightarrow H_2^+(X\,^2\Sigma_g^+, v')$ ionisation energies for $v'=0$ to 8 are 15.4259, 15.6976, 15.9535, 16.1941 (Herzberg and Jungen 1972), 16.4204, 16.6291, 16.8281, 17.0130, and 17.1851 eV (Peatman 1976). Energy defects, ΔE, for the nearest resonant charge transfer reactions of ^4S, ^2D and ^2P O^+ ions with $H_2(X\,^1\Sigma_g^+, v''=0)$ are given in table 2. The ground $O^+(^4S)$ state reactions are endothermic by 1.808 eV and small cross section values are expected. However, reactions of $O^+(^2D)$ ions are within 0.071 eV of being resonant with the $v'=7$ vibrational level of $H_2^+(X\,^2\Sigma_g^+)$. The $O^+(^2P)$ state ion reactions are within 0.039 eV of being resonant with the $v'=5$ level of $H_2^+(X\,^2\Sigma_g^+)$ and vibrationally excited ions are expected to be produced in reaction (2). Formation of vibrationally excited ($v \geq 3$) product $H_2^+(X\,^2\Sigma_g^+)$ ions have been observed by Rowe *et al* (1980) in thermal $O^+(^2D, ^2P) + H_2(X\,^1\Sigma_g^+, v''=0)$ charge transfer interactions. As a result of this close energy balance between reactants and products in the metastable $O^+(^2D, ^2P)$ reactions, large cross sections are expected and observed at low ion kinetic energies.

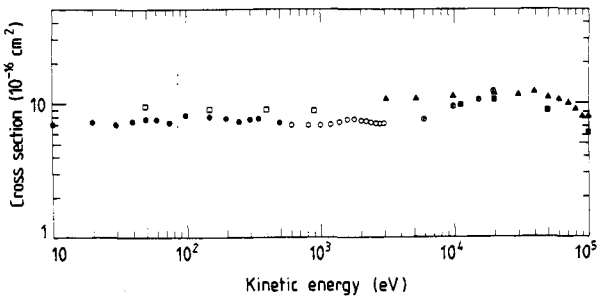

Figure 4. Apparent charge transfer cross sections (10^{-16} cm^2) as a function of reactant ion kinetic energy (eV) in $O^+ + H_2$ reactions for an O^+ beam composed of a mixture of ground and metastable state ions. The full circles at low energies represent data from the present investigation, open squares give data of Gustafsson and Lindholm (1960), open circles give data from Moran and Wilcox (1978), closed squares are the data of Phaneuf *et al* (1978) and triangles and dotted open circles at high energies are data from Hoffman *et al* (1982) and Lockwood *et al* (1978) respectively.

Table 2. Energy defects for charge transfer O^+-H_2 reactions. The nearest energy resonant channels for the reactions below are underlined.

v'	ΔE (eV)[a]	ΔE (eV)[b]	ΔE (eV)[c]
0	<u>1.8078</u>	−1.5161	−1.2421
1	2.0795	−1.2444	−0.9705
2	2.3354	−0.9885	−0.7146
3	2.5760	−0.7479	−0.4740
4	2.8023	−0.5216	−0.2477
5	3.0110	−0.3129	<u>−0.0390</u>
6	3.2100	−0.1139	0.1600
7	3.3949	<u>0.0710</u>	0.3449
8	3.5670	0.2431	0.5170

[a] Energy defects for charge transfer reaction
$O^+(^4S) + H_2(X\,^1\Sigma_g^+, v''=0) \rightarrow O(^3P) + H_2^+(X\,^2\Sigma_g^+, v')$.
[b] Energy defects for charge transfer reaction
$O^+(^2D) + H_2(X\,^1\Sigma_g^+, v''=0) \rightarrow O(^3P) + H_2^+(X\,^2\Sigma_g^+, v')$.
[c] Energy defects for charge transfer reaction
$O^+(^2P) + H_2\,(X\,^1\Sigma_g^+, v''=0) \rightarrow O(^1D) + H_2^+(X\,^2\Sigma_g^+, v')$.

Analogous $O^+(^2D)$ and $O^+(^2P)$ state charge transfer reactions with $N_2\,(X\,^1\Sigma_g^+, v''=0)$ have been measured recently (Lavollée and Henri 1989) using synchrotron radiation threshold photoelectron photoion coincidence techniques. The energies liberated in the $O^+(^2D) \rightarrow O(^3P)$ and $O^+(^2P) \rightarrow O(^1D)$ recombination processes are in close energy balance (+0.02 eV and −0.03 eV) with the $v=1$ and 0 levels of product $N_2^+(A\,^2\Pi)$ ions and cross section in the range of $15\text{-}25\times10^{-16}$ cm^2 were measured at low ion kinetic energies.

The various data sets of figures 2-4 show the general trend of the cross sections over a wide range of energies. The behaviour is very similar to our observations (Xu *et al* 1990) of ground and metastable-state C^+ ion neutralisation in H_2. The most striking feature is that the cross section for metastable $O^+(^2D, ^2P)$ ions at low energies exceeds that for the $O^+(^4S)$ ground-state ions by an order of magnitude.

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