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One-electron capture in collisions of 6–100 keV protons with oxygen atoms

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Abstract. A crossed-beam technique incorporating time-of-flight analysis and coincidence counting of the collision products has been used to study one-electron capture by 6–100 keV protons in collisions with oxygen atoms. In these measurements, ground-state oxygen atoms were provided by an iridium tube furnace dissociation source. The measurements extend the energy range of previous experiments and, for the first time, provide separate cross sections ${}_{10}\sigma_{01}$ for the simple charge transfer process (which is dominated by accidentally resonant one-electron capture) and ${}_{10}\sigma_{02}$ for the transfer ionization process leading to O^{2+} formation. The present cross sections were obtained using a technique and normalization procedure different from all previous measurements. In particular, our measured values of ${}_{10}\sigma_{01}$ are in good accord with previous 0.04–10 keV data by Stebbings *et al* based on a modulated crossed-beam technique but at variance with the considerably smaller values in the range 2.5–25 keV obtained by Williams *et al* using a furnace target method. While our values of ${}_{10}\sigma_{01}$ decrease with increasing energy over the range considered, transfer ionization cross sections pass through a peak value at 34 keV where this process accounts for about 9% of the total one-electron capture cross section rising to 17.5% at 100 keV.

1. Introduction

Atomic oxygen is a primary constituent of the Earth's upper atmosphere and a detailed understanding of the complex way it interacts with the electrons, ions and neutral species present at different altitudes is of considerable importance. Collisions between protons and oxygen atoms are important over a wide energy range. In addition to the proton component of the solar wind, which has an average energy of about 1 keV, much more energetic protons arise as a result of solar flares (cf Johnson 1990).

One-electron capture in H^+–O collisions is of special interest since, at low energies, the simple charge transfer process (with a cross section ${}_{10}\sigma_{01}$)

$$H^+ + O(2s^2 2p^4)\ {}^3P \rightarrow H + O^+ \tag{1}$$

is accidentally resonant for capture of a 2p electron leading to ground-state products, and therefore provides the dominant contribution to the total one-electron capture cross section σ_{10}. At sufficiently high energies, contributions from the transfer ionization process

$$H^+ + O \rightarrow H + O^{2+} + e \tag{2}$$

(with cross section ${}_{10}\sigma_{02}$) might be expected to become significant where $\sigma_{10} = ({}_{10}\sigma_{01} + {}_{10}\sigma_{02})$. In the upper atmosphere, GEOS satellite data (Geiss *et al* 1978) have indicated local concentration ratios O^{2+}/O^+ at times as high as 30%.

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Previous experimental studies of electron capture in H^+–O collisions have been confined to energies below a few keV where measured total cross sections $\sigma_{10} \approx {}_{10}\sigma_{01}$. In the present work we have adapted a crossed-beam technique developed previously in this laboratory (Shah and Gilbody 1981) for studies of collisions involving hydrogen atoms. The method, which we have since used in several different variants for studies of collisions involving both stable and unstable species, utilizes time-of-flight analysis and coincidence counting of the collision products. In this work, as in our recent studies of the electron-impact ionization of O atoms (Thompson *et al* 1995), an iridium tube furnace has been used to provide a thermal energy beam of partially dissociated oxygen. Measurements have been carried out within the range 6–100 keV and separate cross sections ${}_{10}\sigma_{01}$ and ${}_{10}\sigma_{02}$ have been obtained for the first time.

The measurements of σ_{10} by Stebbings *et al* (1964) in the energy range 0.04–10 keV used a modulated crossed-beam technique employing an RF discharge source of partially dissociated oxygen. Care had to be taken to try to ensure that these measurements were not distorted by the presence of unknown fractions of both metastable O atoms and O_2 molecules in the beam from the RF source (Stebbings *et al* 1963). The use of an iridium tube furnace (Fite and Irving 1972) to provide partially dissociated oxygen beams in the ground state avoids such uncertainties. Rutherford and Vroom (1974), using a modulated crossed-beam technique with an oxygen beam derived from an iridium tube furnace, were able to obtain cross sections σ_{10} at energies within the range 1–500 eV. In a different experimental approach, Williams *et al* (1984) in this laboratory used an iridium furnace to provide a target of partially dissociated oxygen. Measurements of the degree of neutralization of a proton beam directed through the furnace allowed measurements of σ_{10} in the range 2.5–25 keV. Williams *et al* (1984) obtained values which were only about 50% of the cross sections measured by Stebbings *et al* (1964) in the energy range of overlap, a difference they suggested might be attributable to the influence of metastables in the experiment of Stebbings *et al* (1964). However, a more recent crossed-beam experiment by Van Zyl and Steven (1991) in the range 0.12–2.0 keV using an iridium tube furnace source and measurements by Lindsay *et al* (1995) at energies of 0.5, 1.5 and 5 keV using a microwave discharge as a target, both provide values of σ_{10} which are in reasonable accord with those of Stebbings *et al* (1964). Our present measurements, which are based on an experimental approach and calibration procedure different from all the previous work, as well as providing data in an extended energy range for both simple charge transfer and transfer ionization, have allowed us to check on the serious discrepancy between the results of Williams *et al* (1984) and Stebbings *et al* (1964).

2. Experimental approach

2.1. General description

The basic apparatus and measuring procedure was similar to that described in our previous measurements of ionization and charge transfer in collisions involving both atomic and molecular hydrogen (Shah and Gilbody 1981, 1982, 1983) so that only a brief outline of the essential features is necessary here.

A momentum-analysed beam of protons of selected energy within the range 6–100 keV was arranged to intersect (at right angles) a thermal energy beam of partially dissociated oxygen in a differentially pumped region maintained at a pressure of about 2×10^{-7} Torr. The arrangement of the iridium tube furnace used to provide the oxygen beam was similar to that used in our recent studies of the electron-impact ionization of atomic oxygen (Thompson *et al* 1995). The tube, fabricated from seam-welded iridium foil, was heated by passing an

alternating current of up to 340 A through it. Oxygen gas, introduced at one end, flowed through at a constant rate and emerged through a 2 mm diameter aperture at the mid-point of the hot central region. Although dissociation fractions of up to 0.9 could be obtained at low gas flow rates, in these measurements (as in our previous work) it was necessary to use higher gas flow rates in order to obtain acceptable signal-to-background ratios, dissociation fractions were usually about 0.5. The furnace temperature was determined by means of an optical pyrometer.

Slow ions and electrons formed as collision products in the crossed-beam region were swept out by a transverse electric field of up to 75 V cm^{-1} applied between two high-transparency grids located on either side of the crossed-beam region. As in our previous work, particular care was taken to ensure that the small deflection of the primary beam produced by this field caused a negligible change in the effective collision volume. The slow extracted product ions were further accelerated by passage through a second grid and were then recorded by a particle multiplier. O^{n+} ions could be identified and distinguished from O_2^+ and background product ions by their characteristic times of flight to the multiplier in accordance with their charge to mass ratios.

In order to distinguish the O^+ and O^{2+} ions arising from (1) and (2) from those arising from the pure ionization process

$$H^+ + O \rightarrow H^+ + O^{n+} + ne \tag{3}$$

the fast H atoms formed by one-electron capture were counted in coincidence with the O^+ and O^{2+} ions arising from the same events. Beyond the interaction region, the fast H atom component of the primary beam formed by electron capture was separated from the ion

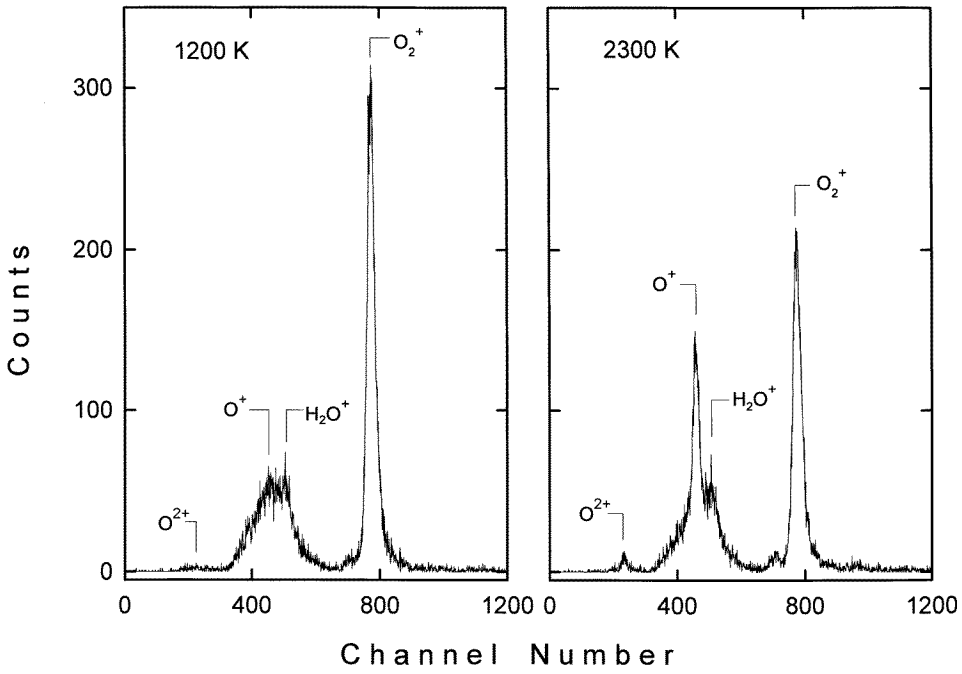

Figure 1. Slow ion–fast H atom time-of-flight coincidence spectrum for one-electron capture by 30 keV protons in oxygen produced by an iridium tube furnace at temperatures of 1200 K and 2300 K.

component by electrostatic deflection and recorded by a particle counter (see figure 1 of the paper by Shah and Gilbody 1982). In this counter, secondary electrons released from a metal target plate upon which the fast H atoms impinged, were accelerated and recorded as pulses by a particle multiplier.

A time-to-amplitude converter operated with start pulses from the fast neutral beam and stop pulses from the slow ion product counter after an appropriate delay allowed a slow ion–fast H atom coincidence spectrum to be obtained. Figure 1 shows a typical coincidence spectrum obtained with the iridium furnace at 2300 K when the beam was partially dissociated and at 1200 K when the beam was entirely molecular. Production of O^{n+} ions for $n > 2$ was found to be insignificant for the primary ion beam energies considered. Relative cross sections for (1) and (2) at different primary beam energies were determined by comparing the coincidence count rates for the same oxygen target beam conditions.

2.2. Calibration and normalization procedure

The cross sections ${}_{10}\sigma_{01}$ for the simple charge transfer process (1) and ${}_{10}\sigma_{02}$ for the transfer ionization process (2) may be expressed as

$$ {}_{10}\sigma_{0n} = S_T(O^{n+})/k\mu \tag{4}$$

where $S_T(O^{n+})$ is the H–O^{n+} coincidence signal per unit primary beam intensity with the furnace at a high temperature T, μ is the effective thickness of the O atom beam and the constant k reflects the overall detection efficiency of the collision products. It was essential to make accurate allowance, as described in our previous work on H^+–H collisions (Shah and Gilbody 1981), for contributions to the observed H–O^+ signal from interactions with the background gas (particularly from the incompletely resolved H_2O^+ peak) and from dissociative electron capture in H^+–O_2 collisions. In spite of the differential pumping, a small increase in pressure also occurs in the crossed-beam region when O_2 is admitted to the furnace and this also leads to an increase in the signal contribution from O_2 molecules.

With the furnace operated at our standard low temperature of $T_0 = 1200$ K, when the beam is entirely molecular, the total H–O^{n+} coincidence signal per unit primary beam current is given by

$$ S_0^{n+} = S_0^{\mathrm{D}}(O^{n+}) + S_{\mathrm{B}} \tag{5}$$

where $S_0^{\mathrm{D}}(O^{n+})$ is the contribution arising from dissociative ionization of O_2 molecules present in the beam and the crossed-beam region while S_{B} is the background contribution arising from incompletely resolved products of dissociative ionization of residual gases and vapours. When the furnace was operated at our usual high temperature of 2300 K, the observed total H–O^{n+} coincidence signal per unit primary ion beam current may be expressed as

$$ S_T^{n+} = S_T(O^{n+}) + S_T^{\mathrm{D}}(O^{n+}) + S_{\mathrm{B}} \tag{6}$$

in terms of the respective contributions from the O and undissociated O_2 components of the beam and the background gas.

By comparing the H–O_2^+ coincidence signals $S_T(O_2^+)$ and $S_0(O_2^+)$ at respective furnace temperatures T and T_0, the contribution $S_T^{\mathrm{D}}(O^{n+})$ in (6) can be obtained from the relationship

$$ S_T^{\mathrm{D}}(O^{n+}) = S_0^{\mathrm{D}}(O^{n+})S_T(O_2^+)/S_0(O_2^+)\,. \tag{7}$$

The residual gas contribution to both $S_T(O_2^+)$ and $S_0(O_2^+)$ was negligible.

Equations (5) and (6) then allow determination of $S_T(O^{n+})$ which is required in (3) for cross section determination. The product $k\mu$ in equation (3) was effectively determined by normalizing our relative cross sections ${}_{10}\sigma_{01}$ and ${}_{10}\sigma_{02}$ to our recently measured cross sections for electron-impact ionization (Thompson *et al* 1995) which in turn were normalized to the absolute values of Brook *et al* (1978). This normalization procedure was similar to that used in our previous studies of e–H and H^+–H impact ionization (Shah *et al* 1987) so that only the essential features need be summarized here. The method involved the substitution of an electron beam for the proton beam while the oxygen beam conditions remained unchanged. An electron gun was fitted onto a sliding mount so that the electron beam could be moved into the position normally occupied by the proton beam. As described previously (Shah *et al* 1987) the electron and proton beams were both pulsed at a repetition rate of 10^5 s^{-1} and duration 200 ns. Slow O^+ products formed in the beam intersection region were swept out with high efficiency by means of a pulsed electric field applied to the grids immediately after the transit of each primary beam pulse through the oxygen beam. The O^+ ions were identified by time-of-flight spectroscopy and counted by the particle multiplier. In the present work, normalization was carried out by comparing the O^+ signal obtained with an electron beam at 219 eV (the ionization cross section for which is known) with the O^+ signal obtained for H^+ ions in the range 6–30 keV. In this energy range, a comparison of the total O^+ yield with the O^+–H coincidence yield confirmed that O^+ arises predominantly from one-electron capture rather than from pure ionization. As in our previous work (Thompson *et al* 1995), in this normalization, we used the absolute values of electron-impact ionization of O measured by Brook *et al* (1978) after applying the +2.4% correction stipulated by Montague *et al* (1984).

3. Results and discussion

Table 1 shows our measured values of ${}_{10}\sigma_{01}$ and ${}_{10}\sigma_{02}$ for the simple charge transfer process (1) and the transfer ionization process (2) in the respective energy ranges 6–100 keV and 12–100 keV. Uncertainties associated with individual cross sections are assessed at the 67% confidence level and reflect the degree of reproducibility of the values in terms of the various experimental parameters and statistical fluctuations. All these cross sections are subject to an additional estimated uncertainty of ±10% in absolute value as a consequence of our normalization procedure.

Figure 2 shows the present values of ${}_{10}\sigma_{01}$ compared with previous measurements of the one-electron capture cross section σ_{10}. The data of Williams *et al* (1984) and of Stebbings *et al* (1964) in the respective ranges 2.5–25 keV and 0.04–10 keV overlap the present energy range. The other measurements have been confined to energies below our 6 keV lower limit where $\sigma_{10} \approx {}_{10}\sigma_{01}$. The crossed-beam measurements of Stebbings *et al* (1964), Rutherford and Vroom (1974) and Van Zyl and Steven (1991) in the respective energy ranges 0.04–10 keV, 1–500 eV and 0.12–2 keV provided cross section ratios $\sigma_{10}(O)/\sigma_{10}(O_2)$ from which the cross sections in O could be obtained from a knowledge of the corresponding values in O_2. While the cross sections measured by Rutherford and Vroom (1974) are in good agreement with the measurements of Stebbings *et al* (1964), the values obtained by Van Zyl and Steven (1991) are about 20% larger, a result which they suggest reflects the use of different $\sigma_{10}(O_2)$ data for normalization. The very recent results obtained by Lindsay *et al* (1995) at 0.5, 1.5 and 5.0 keV were actually obtained by integration of measured differential cross sections for electron capture over the angular range 0.01–2.26°. The use of a microwave discharge target, which contained O, O_2 and H_2O and smaller amounts of N_2 and CO as well as the possibility of excited species, complicated the derivation of

Table 1. Cross sections ${}_{10}\sigma_{01}$ for simple charge transfer and ${}_{10}\sigma_{02}$ for transfer ionization.

Energy (keV)	${}_{10}\sigma_{01}$ (10^{-16} cm^2)	Energy (keV)	${}_{10}\sigma_{02}$ (10^{-17} cm^2)
6.0	8.04 ± 0.64	—	—
7.0	7.60 ± 0.61	—	—
8.0	7.23 ± 0.58	12.0	1.9 ± 0.4
9.0	7.22 ± 0.51	13.0	1.8 ± 0.4
10.0	7.41 ± 0.59	14.0	2.7 ± 0.5
11.0	6.88 ± 0.55	15.0	2.4 ± 0.5
13.0	6.74 ± 0.54	16.0	2.5 ± 0.5
15.0	6.51 ± 0.52	18.0	3.2 ± 0.6
17.0	6.07 ± 0.49	20.0	3.4 ± 0.6
20.0	5.91 ± 0.47	22.0	3.6 ± 0.6
23.0	5.47 ± 0.48	24.0	3.7 ± 0.7
26.0	5.07 ± 0.45	27.0	3.8 ± 0.6
30.0	4.79 ± 0.38	30.0	3.8 ± 0.6
34.0	4.03 ± 0.36	34.0	4.0 ± 0.6
40.0	3.46 ± 0.25	40.0	3.4 ± 0.6
46.0	3.13 ± 0.28	46.0	3.7 ± 0.6
53.0	2.37 ± 0.21	53.0	2.9 ± 0.5
61.0	2.05 ± 0.18	61.0	2.7 ± 0.5
70.0	1.93 ± 0.17	70.0	2.7 ± 0.5
80.0	1.54 ± 0.14	80.0	2.3 ± 0.4
90.0	1.66 ± 0.10	90.0	2.5 ± 0.4
100.0	1.06 ± 0.10	100.0	2.1 ± 0.4

these cross sections. Nevertheless, their results can be seen to be in good accord with the measurements of Stebbings *et al* (1994). Our present values of ${}_{10}\sigma_{01}$ can also be in satisfactory accord with the measurements of Stebbings *et al* (1964) and the general trend of the other low energy data which generally agree to within the maximum combined experimental uncertainties. The measurements of Williams *et al* (1984) are clearly greatly at variance with the present and all previous data. While we cannot identify the reason for an error in the furnace target method used by Williams *et al* (1984), it seems likely that the assumption of thermodynamic equilibrium within the furnace under the conditions used was unjustified thereby leading to serious errors in the estimated O target densities.

Figure 3 shows the present values of the cross sections ${}_{10}\sigma_{01}$ and ${}_{10}\sigma_{02}$ for simple charge transfer and transfer ionization. The transfer ionization cross sections can be seen to attain a broad maximum at energies near 34 keV where the cross section ratio ${}_{10}\sigma_{02}/\sigma_{10} \approx 0.09$; at 100 keV this ratio rises to 0.17. It is also interesting to note that our measured peak value of 4.0×10^{-17} cm^2 of the transfer ionization cross section ${}_{10}\sigma_{02}$ (which leads to O^{2+} production) is more than an order of magnitude larger than the peak value of the cross section for double ionization by electron impact (5.1×10^{-18} cm^2 at 190 eV) observed previously (Thompson *et al* 1995).

In the case of the simple charge transfer cross section ${}_{10}\sigma_{01}$, the accidental resonant character of the 2p electron capture process, which leads to a $\sigma^{1/2} = a - b \log E$ energy dependence at low energies, is well known (cf Stebbings *et al* 1964). In the present energy range, while the cross section continues to decrease with increasing energy, there is evidence of a broad 'bulge' in the cross section curve above 10 keV. It is possible that this reflects the additional possibility of capture of a 2s electron which might be expected to become significant at these higher energies. The energy required to remove a 2s electron is about double that required to remove a 2p electron. It is also interesting to note that the peak

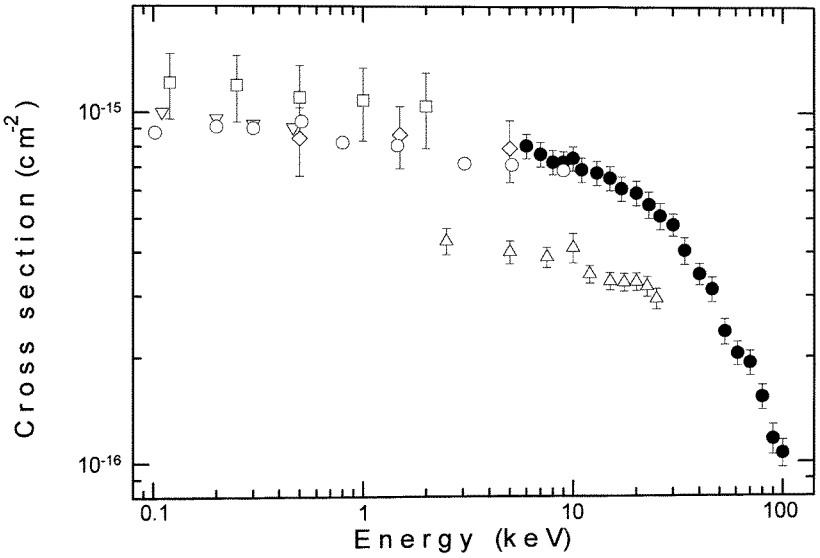

Figure 2. Cross sections for one-electron capture by protons in collisions with oxygen atoms. (●) Cross sections ${}_{10}\sigma_{01}$ for simple charge transfer, present data. (△) Cross sections $\sigma_{10} \approx {}_{10}\sigma_{01}$, Williams *et al* (1984). (▽) Cross sections $\sigma_{10} \approx {}_{10}\sigma_{01}$, Rutherford and Vroom (1974). (○) Cross sections $\sigma_{10} \approx {}_{10}\sigma_{01}$, Stebbings *et al* (1964). (◊) Cross sections $\sigma_{10} \approx {}_{10}\sigma_{01}$, Lindsay *et al* (1995). (□) Cross sections $\sigma_{10} \approx {}_{10}\sigma_{01}$, Van Zyl and Steven (1991).

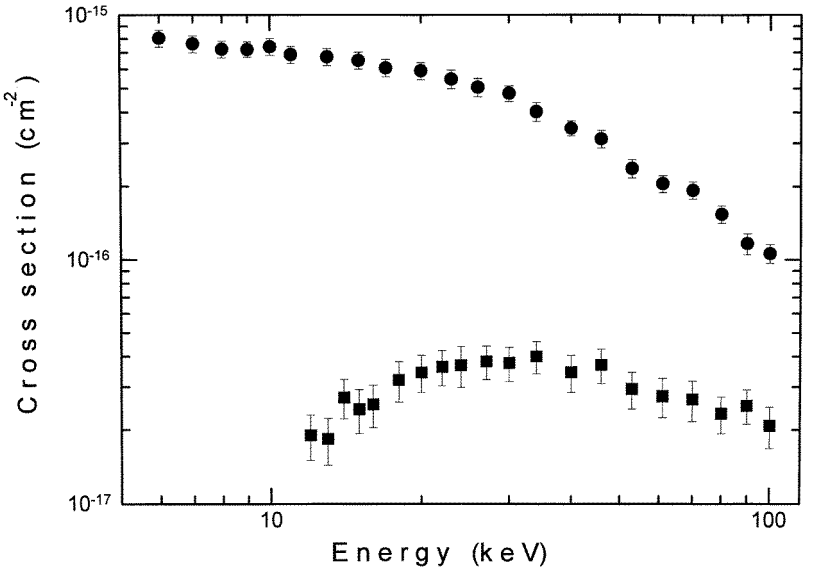

Figure 3. Present cross sections ${}_{10}\sigma_{01}$ for simple charge transfer (shown as ●) and ${}_{10}\sigma_{02}$ for transfer ionization (shown as ■).

in the transfer ionization cross section ${}_{10}\sigma_{02}$ occurs in the same energy region as the broad bulge in ${}_{10}\sigma_{01}$. As in the case of capture of a 2p electron, capture of a 2s electron can be accompanied by electron ejection through binary collisions leading to the O^{2+} ions observed

in (2). This type of process has been shown to be an effective mechanism for the production of multiply charged ions (Shah *et al* 1995).

4. Conclusions

In the present work, a crossed-beam coincidence technique incorporating time-of-flight analysis and coincidence counting of the collision products has been used to obtain cross sections for one-electron capture by 6–100 keV protons in collisions with atomic oxygen. The measurements extend the energy range of previous studies. Separate cross sections ${}_{10}\sigma_{01}$ for simple charge transfer and ${}_{10}\sigma_{02}$ for transfer ionization leading to O^{2+} formation have been obtained for the first time in the respective energy ranges 6–100 keV and 12–100 keV. Our measured values of ${}_{10}\sigma_{01}$ are in good general accord with previous lower energy measurements using several different methods. The present values of ${}_{10}\sigma_{01}$, like the previous lower energy measurements, are at variance with the measurements of Williams *et al* (1984) based on a furnace target approach. Our results, which are based on a method and normalization procedure different from all previous measurements indicate that the results of Williams *et al* (1984) are incorrect. Our results also show that the cross section ratio ${}_{10}\sigma_{02}/\sigma_{10}$ increases from about 0.09 at 34 keV, where ${}_{10}\sigma_{02}$ attains a peak value, to 0.17 at our high-energy limit of 100 keV. In addition, the peak value of ${}_{10}\sigma_{02}$ is more than an order of magnitude greater than the peak value of the cross section for double ionization by electron impact, a result which might be significant in the interpretation of O^{2+} production in the upper atmosphere.

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