# Charge transfer cross sections in collisions of ground state $O^+(^4S)$ ions with $H_2$ and various carbon-containing molecules in the low-energy region

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## **Abstract**

Charge transfer cross sections of the ground state  $O^+(^4S)$  ions with  $H_2$ , CO,  $CO_2$ ,  $CH_4$ ,  $C_2H_2$ ,  $C_2H_6$  and  $C_3H_8$  molecules have been measured using an initial growth rate method in the energy range 0.2–4.5 keV. In the present experiment, the ground state  $O^+(^4S)$  ions have been produced by carefully energy-controlled electron impact to avoid the influence of the metastable  $O^{+*}(^2D, ^2P)$  state ions. The observed cross sections are compared with calculations based on a formula developed by Olson. The energy dependence of the present cross sections for  $H_2$  molecules shows a minimum at around 2 keV. The present experimental results for CO and  $CO_2$  molecules are slightly different from previous measurements. For hydrocarbon molecules, where no experimental data are available so far, both the present experimental and calculated results are in good agreement with each other, if product molecular ions are assumed to be in some vibrationally excited states.

#### 1. Introduction

The oxygen atom is one of the most common elements in the atmosphere and the ionosphere of the Earth. This circulates through chemical reactions in the atmosphere and photosynthesis of plants and is indispensable to the existence and activities of life. Oxygen is also one of the typical impurities in almost all laboratory plasmas. In fact, among many interactions involving oxygen, charge transfer collisions between singly charged oxygen O<sup>+</sup> ions and

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various carbon-containing molecules are relevant to the low-temperature edge plasma region of current thermonuclear fusion devices (Janev 1995). Needless to say, the processes involving CO and CO<sub>2</sub> also constitute an important part in many reactions in interstellar and ionospheric matter (Dalgarno 1990). Recently, oxygen ions in various charge states have been observed in the tails or comas of comets such as Halley and Hyakutake (Fuselier *et al* 1991) which are now believed to consist mainly of hydrocarbon molecules. Also x-rays from highly charged oxygen ions have been observed and are understood to be due to charge transfer (Lisse *et al* 1996).

However, cross section measurements in charge transfer processes of O<sup>+</sup> ions colliding with carbon-containing molecules are scarce (Gustafsson and Lindholm 1960, Rutherford and Vroom 1976, Moran and Wilcox 1978, Flesch and Ng 1991a, Lindsay *et al* 1999), though there are some experimental data for H<sub>2</sub> molecules. Moreover, two contradictary data sets exist in O<sup>+</sup> + H<sub>2</sub> collisions. Xu *et al* (1990) measured the charge transfer cross sections for both the ground state O<sup>+</sup>( $^4$ S) ions and metastable state O<sup>+\*</sup>( $^2$ D,  $^2$ P) ions in collisions with H<sub>2</sub> molecules in the lower-energy region. Their cross sections for the ground state O<sup>+</sup>( $^4$ S) ions seem to be too small compared with other data and cannot be connected with our previous results. Irvine and Latimer (1991) also presented experimental data for this collision using a photo-ionization ion source and supported the results of Xu *et al* (1990). Furthermore, measurements by Flesh and Ng (1991b), combining a photo-ionization ion source and an octopole ion beam guide technique, show a rapid decrease of the cross sections at energies below  $\sim$  50 eV. On the other hand, very recently, Sieglaff *et al* (1999) measured these cross sections with the 'beam-filtering' and beam attenuation methods, and their cross section values are very close to our previous data (Kusakabe *et al* 1990b).

Since the electron capture processes at low energies are known to be strongly dependent upon the internal electronic energy/state of collision partners, metastable excited state ions, if present in the primary ion beam, may sometimes significantly influence the observed cross sections of charge transfer processes. Over the past few years, we have measured the charge transfer cross sections for  $C^+$ ,  $N^+$  and  $O^+$  ions in collisions with  $H_2$  molecules and  $H_2$  atoms, and have found that metastable state ions indeed enhance the observed cross sections (Kusakabe *et al.* 1990b), sometimes by an order of magnitude.

On the other hand, theoretical approaches applicable to slow ion–molecule collisions are also few in number. Kimura and Lane (1989) have developed a molecular-orbital (MO) expansion method taking into account the molecular orientation with respect to the incident ion direction (Kimura *et al* 1995, 1996). In our previous studies for H<sup>+</sup> and C<sup>+</sup> ions in collisions with H<sub>2</sub>, CO, CH<sub>4</sub> and C<sub>2</sub>H<sub>2</sub> molecules, their theoretical calculations have been found to be in good agreement with the measurements (Kusakabe *et al* 1999, 2000a, 2000b). Olson (1972) derived a simple formula for evaluating the charge transfer cross sections for singly charged ion–atom collisions based on a Demkov-type approximation. This formula is known to give a reasonably good picture of the gross features even for molecular targets, and has been used successfully to guide experimental studies (Kusakabe *et al* 1999, 2000a, 2000b).

As a continuation of our effort, in this paper, we have measured the charge transfer cross sections for the ground state O<sup>+</sup>(<sup>4</sup>S) ions colliding with H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> molecules at low kinetic energies. In particular, in the present experiments, the ion source is much more carefully controlled than in the previous case (Kusakabe *et al* 1990b) in order to avoid the influence of the metastable state ions. Thus we determine the cross sections for the ground state ions in the energy range 0.2–4.5 keV by applying an initial growth rate method to the oxygen atom produced by charge transfer. The formula presented by Olson (1972) is used to estimate the cross sections and is compared with the present experimental results.

**Table 1.** Charge transfer processes investigated and their energy defects.

Process	Energy defect <sup>a</sup> (eV)	Number
(a) All in their ground states before and after collision		
$O^{+}(^{4}S) + H_{2} (v_{i} = 0) \rightarrow O(^{3}P_{2}) + H_{2}^{+} (v_{f} = 0)$	-1.81	(1)
$O^{+}(^{4}S) + CO(v_{i} = 0) \rightarrow O(^{3}P_{2}) + CO^{+}(v_{f} = 0)$	-0.396	(2)
$O^{+}(^{4}S) + CO_{2} (v_{i} = 0) \rightarrow O(^{3}P_{2}) + CO_{2}^{+} (v_{f} = 0)$	-0.162	(3)
$O^{+}(^{4}S) + CH_{4} (v_{i} = 0) \rightarrow O(^{3}P_{2}) + CH_{4}^{+} (v_{f} = 0)$	0.638	(4)
$O^{+}(^{4}S) + C_{2}H_{2} (v_{i} = 0) \rightarrow O(^{3}P_{2}) + C_{2}H_{2}^{+} (v_{f} = 0)$	2.22	(5)
$O^{+}(^{4}S) + C_{2}H_{6} (v_{i} = 0) \rightarrow O(^{3}P_{2}) + C_{2}H_{6}^{+} (v_{f} = 0)$	2.10	(6)
$O^{+}(^{4}S) + C_{3}H_{8} (v_{i} = 0) \rightarrow O(^{3}P_{2}) + C_{3}H_{8}^{+} (v_{f} = 0)$	2.67	(7)
(b) Excited product atom after collision		
$O^{+}(^{4}S) + C_{2}H_{2} (v_{i} = 0) \rightarrow O^{*}(^{1}D) + C_{2}H_{2}^{+} (v_{f} = 0)$	0.251	(8)
$O^{+}(^{4}S) + C_{2}H_{6} (v_{i} = 0) \rightarrow O^{*}(^{1}D) + C_{2}H_{6}^{+} (v_{f} = 0)$	0.131	(9)
$O^{+}(^{4}S) + C_{2}H_{6} (v_{i} = 0) \rightarrow O^{*}(^{1}S) + C_{2}H_{6}^{+} (v_{f} = 0)$	-2.09	(10)
$O^{+}(^{4}S) + C_{3}H_{8} (v_{i} = 0) \rightarrow O^{*}(^{1}D) + C_{3}H_{8}^{+} (v_{f} = 0)$	0.701	(11)
$O^{+}(^{4}S) + C_{3}H_{8} (v_{i} = 0) \rightarrow O^{*}(^{1}S) + C_{3}H_{8}^{+} (v_{f} = 0)$	-1.52	(12)

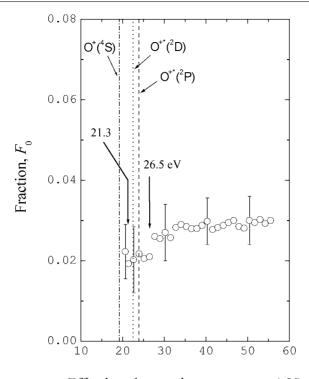
<sup>&</sup>lt;sup>a</sup> Each energy defect was calculated using the ionization energy of the target molecule (Lide 1999) and energy levels of the oxygen atom (Bashkin and Stoner 1975). Note that  $v_i$  and  $v_f$  are the initial and final vibrational quantum numbers of the target molecule, respectively.

The following specific processes shown in table 1 are considered in the present study where not only the ground state but also some excited states of neutral product oxygen atoms are taken into account. Here the energy defect is defined as the internal energy difference before and after collisions. In the collision processes (1)–(7), all the collision partners involved are assumed to be in their ground states before and after collisions. Among them, the collision processes (1)–(3) are endothermic. The exothermic reactions (4)–(7) give the quasi-resonant charge transfer if some vibrational excited states of the product molecular ions are involved. This situation is similar to H<sup>+</sup> collisions (Kusakabe et al 1999, 2000a, 2000b) because the ionization energy of the ground state O(2p<sup>4</sup> <sup>3</sup>P<sub>2</sub>) atom (13.61806 eV) is very close to that of the ground state H (1s <sup>2</sup>S) atom (13.598 44 eV) (Bashkin and Stoner 1975). One of the differences between oxygen and hydrogen atoms is that two low-lying hyperfine states of O(2p<sup>4</sup> <sup>3</sup>P<sub>1</sub>) and O(2p<sup>4</sup> <sup>3</sup>P<sub>0</sub>) are present with energies very close to that of the ground state oxygen atom (13.598 43 and 13.589 91 eV, respectively) (Bashkin and Stoner 1975). Another important difference is that the charge transfer processes (8)–(12) to the excited states (<sup>1</sup>D, <sup>1</sup>S) of the oxygen atom can occur in O<sup>+</sup> ion collisions with relatively high probabilities. Among them, the exothermic reactions (8), (9) and (11) can also involve quasi-resonant charge transfer if the product molecular ions are in vibrationally excited states.

#### 2. Experimental method

As the experimental apparatus and methods used in the present investigation are essentially the same as in the previous ones (Kusakabe *et al* 1990a, 1990b, 1999, 2000a, 2000b), a brief outline and a few different points are given.

An oxygen ion beam was extracted from a conventional electron impact ion source. A target gas of high purity (>99.9%) was used and its pressure in a 4 cm long collision cell was measured with a calibrated Pirani gauge (Kusakabe *et al* 1998). After charge-transfer collisions, the oxygen ions and atoms emerging from the cell were clearly separated with an electrostatic deflector and were detected using a position-sensitive detector consisting of a microchannel plate and a resistive anode (MCP-PSD) (Kusakabe *et al* 1993). Their fractions



Effective electron impact energy (eV)

**Figure 1.** Typical variations of the neutral oxygen atom fraction  $F_0$  produced for 2.0 keV O<sup>+</sup> ions colliding with H<sub>2</sub> molecules versus the effective impact-electron energy  $E_e$ . The target gas pressure of H<sub>2</sub> is  $\sim 0.1$  Pa. The vertical lines show the threshold energies for processes (13)–(15).

were determined from peak areas in the charge spectrum as a function of the target gas thickness (Kusakabe *et al* 2000b). The charge transfer cross sections were derived based upon the growth rate method by fitting the observed fraction  $F_0$  of neutral oxygen atoms formed in the charge transfer collisions to a quadratic function of the target gas thickness. The front and main chambers were evacuated down to a base pressure of less than about  $6 \times 10^{-6}$  Pa with a  $500 \, 1 \, \text{s}^{-1}$  turbo-molecular pump and a  $700 \, 1 \, \text{s}^{-1}$  cryo-pump.

The threshold energies for producing the ground state  $O^+(^4S)$  ions, the metastable  $O^{+*}(^2D)$  and  $O^{+*}(^2P)$  ions from the ground state  $CO_2$  molecules by electron impact,

$$e^- + CO_2 \rightarrow 2e^- + O^+(^4S) + CO$$
 (13)

$$\rightarrow 2e^- + O^{+*}(^2D) + CO$$
 (14)

$$\rightarrow 2e^{-} + O^{+*}(^{2}P) + CO$$
 (15)

are known to be 19.2, 22.5 and 23.9 eV, respectively (Bashkin and Stoner 1975, Lide 1999). The absolute (effective) energy  $E_e$  of the impact electrons in the ion source has been determined through observing the ionization energies of helium and neon atoms and the appearance potentials of C<sup>+</sup> reactant ions from CO, N<sup>+</sup> ions from N<sub>2</sub> and O<sup>+</sup> ions from CO<sub>2</sub>. We have examined the effect of ions in different electronic states for charge transfer cross sections in the present target molecules by measuring the variation of neutral atom fractions  $F_0$  produced through charge transfer as a function of the electron impact energy  $E_e$  in the ion source at a constant target gas density. For example, in 2.0 keV O<sup>+</sup> + H<sub>2</sub> collisions, as shown in figure 1,

the observed fraction  $F_0$  is constant from the threshold up to about 26.25 eV, suggesting that process (13) is dominant there. Then its fraction increases as the electron impact energy increases, though still within the experimental uncertainties. At  $E_e = 50$  eV, the enhancement has been found to be about 25% for 0.3 keV and 50% for 2.0 keV O<sup>+</sup> ions. This increase can be attributable to production of the metastable O<sup>+\*</sup>( $^2$ D) and O<sup>+\*</sup>( $^2$ P) ions in processes (14) and (15). Then, the effective impact energy of electrons was set to 21.3 eV throughout the present cross section measurements. Thus we believe that the observed cross sections correspond mainly to those for the ground state O<sup>+</sup>( $^4$ S) ions.

However, it should be noted that neutral atom fractions produced in various carbon-containing molecule collisions do not change even if  $E_e$  increases up to 50 eV. This situation is somewhat different from that of  $C^+$  ions (Kusakabe *et al* 1999, 2002). In  $C^+$  ion collisions, neutral atom fractions were observed to increase for CO, CO<sub>2</sub> and CH<sub>4</sub> targets as well as in H<sub>2</sub> (and D<sub>2</sub>). Moreover, the increase in  $C^+$  + H<sub>2</sub> collisions is about twice as large as that in  $O^+$ +H<sub>2</sub> collisions. This difference can be attributed to the endothermicity in collisions. When the charge transfer collisions are strongly endothermic, the metastable state ion effectively decreases the energy defect and thus their contribution results in enhanced cross sections. On the other hand, in exothermic reactions, the metastable ions tend to increase the energy defect and are expected to decrease the cross sections. However, this effect may diminish if the vibrational excitation of product molecular ions is taken into account (see the discussion later).

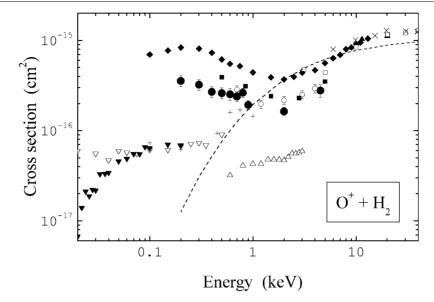
The statistical uncertainty in deriving the cross sections from the fraction curve ranges from a few per cent to 11.5%. The systematic uncertainty including those of the target thickness, the temperature of the gas target, etc is estimated to be from 10.5% to 16.2%. Total experimental uncertainties of the absolute cross sections are determined by the quadratic sum of these uncertainties involved.

#### 3. Results and discussion

The present experimental cross sections for charge transfer of the ground state O<sup>+</sup>(<sup>4</sup>S) ions colliding with various molecules are summarized in table 2. To the best of our knowledge, no cross sections for the hydrocarbon molecules investigated here have been reported so far.

CO <sub>2</sub> , CH <sub>4</sub> , C <sub>2</sub> H <sub>2</sub> , C <sub>2</sub> H <sub>6</sub> and C <sub>3</sub> H <sub>8</sub> molecules.
Cross sections ( $10^{-16} \text{ cm}^2/\text{molecule}$ )

Energy	Cross sections (10 <sup>-16</sup> cm <sup>2</sup> /molecule)						
(keV)	$H_2$	CO	$CO_2$	$CH_4$	$C_2H_2$	$C_2H_6$	$C_3H_8$
0.2	$3.57 \pm 0.49$	$7.19 \pm 1.02$	$36.0 \pm 5.0$	$56.6 \pm 7.8$	$8.66 \pm 1.41$	$52.1 \pm 8.5$	$62.1 \pm 8.6$
0.3	$3.24\pm0.45$	$9.69 \pm 1.36$	$32.0 \pm 4.4$	$44.4 \pm 6.2$	$7.58 \pm 1.33$	$44.8 \pm 7.4$	$53.6 \pm 7.5$
0.4	$2.70 \pm 0.38$	_	_	_	_	_	_
0.5	$2.61 \pm 0.36$	$12.6 \pm 1.8$	$29.9 \pm 4.1$	$37.9 \pm 5.2$	$9.09 \pm 1.48$	$37.8 \pm 6.2$	$46.4 \pm 6.4$
0.6	$2.54 \pm 0.38$	_	_	_	_	_	_
0.7	$2.39 \pm 0.29$	_	_	_	_	_	_
0.8	$2.64 \pm 0.30$	$15.7 \pm 1.7$	$25.8 \pm 2.8$	$36.2 \pm 3.9$	$7.70 \pm 1.29$	$38.4 \pm 6.3$	$43.5 \pm 6.0$
0.9	$1.93 \pm 0.21$	_	_	_	_	_	_
1.2	_	$18.4 \pm 2.0$	$27.0 \pm 2.9$	$28.7 \pm 3.3$	$9.00 \pm 1.24$	$31.7 \pm 5.2$	$40.1 \pm 5.6$
2.0	$1.64 \pm 0.18$	$19.4 \pm 2.1$	$25.2\pm2.8$	$29.5 \pm 3.2$	$10.4 \pm 1.5$	$37.4 \pm 6.2$	$42.7 \pm 4.6$
3.0	_	$18.9 \pm 2.1$	$23.6 \pm 3.6$	$27.7 \pm 3.1$	$11.6 \pm 1.7$	$35.8 \pm 6.0$	$41.4 \pm 4.4$
4.5	$2.79 \pm 0.44$	$19.0 \pm 2.1$	$21.4 \pm 2.4$	$26.9 \pm 2.9$	$14.7 \pm 2.1$	$34.4 \pm 4.8$	$40.9 \pm 4.4$

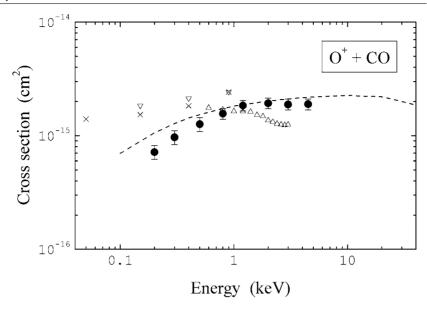


**Figure 2.** Charge-transfer cross sections for O<sup>+</sup> ions in collisions with H<sub>2</sub> molecules. Experiment: 
•, present data;  $\bigcirc$ , previous data (Kusakabe *et al* 1990b); ■, Sieglaff *et al* (1999); +, Irvine and Latimer (1991);  $\blacktriangledown$ , Flesch and Ng (1991b);  $\triangledown$ , Xu *et al* (1990);  $\square$ , Hoffman *et al* (1982); •, Nutt *et al* (1979); △, Phaneuf *et al* (1978); ×, Lockwood *et al* (1978);  $\triangle$ , Moran and Wilcox (1978). Theory: ---, the Olson formula for process (1).

## 3.1. H<sub>2</sub> molecules

The present cross sections for charge transfer in the ground state  $O^+(^4S) + H_2$  collisions are depicted in figure 2 together with data previously published so far (Lockwood *et al* 1978, Moran and Wilcox 1978, Phaneuf *et al* 1978, Nutt *et al* 1979, Hoffman *et al* 1982, Xu *et al* 1990, Flesch and Ng 1991b, Irvine and Latimer 1991, Sieglaff *et al* 1999, Kusakabe *et al* 1990b). In order to check the influence of the ion source operating parameters, we have also made additional measurements at energies 0.4, 0.7, 1.2 and 2.0 keV using  $O^+$  ions produced from  $O_2$  molecules, instead of  $CO_2$  gas, by 20.8 eV electron impact. These results are in good agreement with the present data where  $CO_2$  molecules are used to produce  $O^+$  ions.

Since the collision process (1) is strongly endothermic, the cross sections are expected to decrease rapidly toward lower energies. The Olson formula has been found to reproduce the present experimental data nicely at high energies but shows serious discrepancies at energies below 2 keV as shown in figure 2. This situation is similar to  $C^+ + H_2$  and  $C^+ + CO$  collisions (Kusakabe *et al* 1999). In fact, most of the experimental data decrease down to about 2 keV, though there are some discrepancies among them. This can be mainly due to the contribution of the unknown fraction of metastable state ions in the primary beam. On the other hand, the present data and the data of Sieglaff *et al* (1999), where a careful selection of the ground state oxygen ions was made, tend to increase again below 2 keV, suggesting that other mechanisms may prevail at low energies. This increase could be due to the fact that the slow approach of charged heavy particles may induce the vibration of the target molecule before the electron capture occurs and then the effective ionization energy of the  $H_2$  target decreases, thus resulting in a smaller energy defect. Understanding such behaviour of the cross sections in the low-energy region would require more sophisticated theoretical calculations.



**Figure 3.** Charge-transfer cross sections for  $O^+$  ions in collisions with CO molecules. Experiment:  $\bullet$ , the present data;  $\triangle$ , Moran and Wilcox (1978);  $\times$ , Gustafsson and Lindholm (produced from CO<sub>2</sub>, 1960);  $\nabla$ , Gustafsson and Lindholm (produced from CO, 1960). Theory: ---, the Olson formula for process (2).

## 3.2. CO and CO2 molecules

The present cross sections for  $O^+(^4S) + CO$  collisions are depicted in figure 3 together with other experimental data and the theoretical calculations.

Since collision process (2) is weakly endothermic, the cross sections are expected to decrease toward lower energies. Indeed, the present data show such a trend, which is in contrast to the previous data of Moran and Wilcox (1978) and Gustafsson and Lindholm (1960). Actually, the Olson formula (1972) reproduces the energy dependence of the present data reasonably well, as can be seen in figure 3.

The present measured cross sections for  $O^+(^4S) + CO_2$  collisions, shown in figure 4, decrease as the incident energy increases. The present data are found to be in excellent agreement with those of Lindsay *et al* (1999) and connect smoothly with the data of Flash and Ng (1991a). In contrast, the previous data of Rutherford and Vroom (1976) and Moran and Wilcox (1978) are not consistent with the present data. Although collision process (3) is endothermic, the energy dependence of the present cross sections shows a nearly resonance feature. Since the vibrational energy in the bending mode of the  $CO_2$  molecule is only about three times larger than the thermal energy, this collision system can be nearly resonant. Indeed, the Olson formula shows a tendency that is in agreement with our experimental results, though the calculated cross sections are about 30% larger than the measured values.

#### 3.3. CH<sub>4</sub> molecules

The present cross sections for  $O^+(^4S) + CH_4$  collisions are depicted in figure 5. The present experimental cross sections decrease up to about 1.2 keV as the collision energy increases, and level off above 1.2 keV.

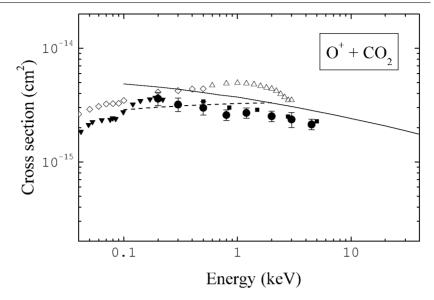
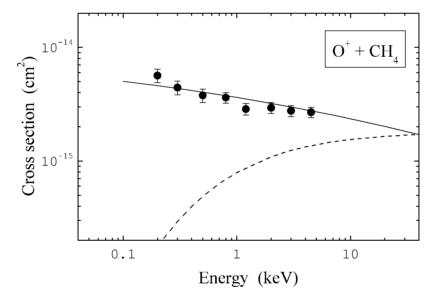


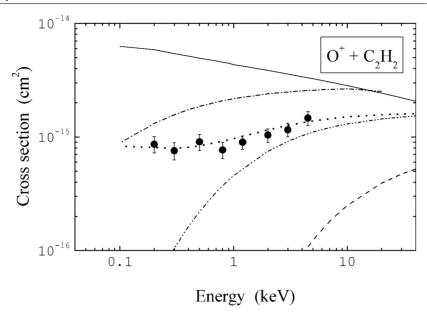
Figure 4. Charge-transfer cross sections for  $O^+$  ions in collisions with  $CO_2$  molecules. Experiment: 

•, the present data; ■, Lindsay *et al* (1999);  $\triangle$ , Moran and Wilcox (1978);  $\blacktriangledown$ , Flesch and Ng (1991a);  $\diamondsuit$ , Rutherford and Vroom (1976). Theory: --, the Olson formula for process (3); ——, the Olson formula for the accidental resonance case.



**Figure 5.** Charge-transfer cross sections for  $O^+$  ions in collisions with CH<sub>4</sub> molecules. Experiment:  $\bullet$ , the present data. Theory: ---, the Olson formula for process (4); ——, the Olson formula for the accidental resonance case.

The calculated results of the Olson formula, assuming that the target molecule is in the vibrationally ground state after collision (corresponding to process (4), see the broken curve in figure 5), are much smaller than our measurements at lower energies. On the other hand, if the vibrational excited states in the product molecular ions are assumed to proceed, then the



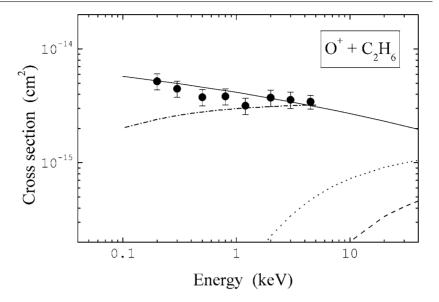
**Figure 6.** Charge-transfer cross sections for  $O^+$  ions in collisions with  $C_2H_2$  molecules. Experiment:  $\bullet$ , the present data. Theory: ---, the Olson formula for process (5); ----, the Olson formula for process (8); ----, the Olson formula for process (5) with vibrational excitation of the product molecular ion; ---, the Olson formula for the accidental resonance case; ----, the Olson formula for process (5) with vibrational excitation of the product molecular ion plus the accidental resonance case.

energy defect of this reaction becomes very small and a nearly resonant condition is expected to be attained. Thus good agreement between the present measurements and calculations (full curve) is obtained.

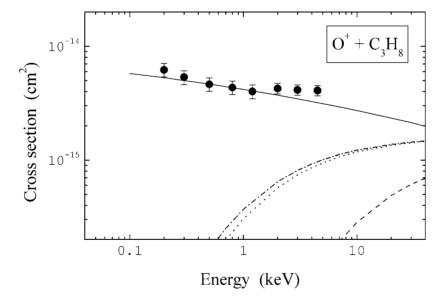
## 3.4. $C_2H_2$ molecules

Figure 6 shows the present cross sections for  $O^+(^4S) + C_2H_2$  collisions. The present experimental results are roughly constant below 0.8 keV and, then, increase slightly as the collision energy increases above 0.8 keV. The calculated results for process (5) (broken curve) using the Olson formula, assuming ground-to-ground state charge transfer, significantly underestimate the measured cross sections by orders of magnitude at low energies. In contrast, the calculated results for process (8) (chain curve), assuming charge transfer into the excited state  $O^*(^1D)$  of the projectile, are larger than the present results. If the vibrational excitation  $(v_f \sim 5)$  of the product target molecular ion is assumed in process (5), the calculated results (double-dotted chain curve) become close to our measurements at energies above 0.8 keV but are still too small at lower energies.

The measured cross sections can consist of not only those due to a single process but also those due to the sum of the contribution of different final channels. The summation of these calculated values with appropriate transition probabilities can be adjusted to our measurements. As an example, the dotted curve in figure 6 represents the calculated cross section of two combined processes, namely 13% the full resonance process (full curve) and 87% the exothermic reaction (5) accompanied with the vibrational excitation ( $v_f \sim 5$ ) of the product target molecular ion (double-dotted chain curve). The calculated results seem to



**Figure 7.** Charge-transfer cross sections for  $O^+$  ions in collisions with  $C_2H_6$  molecules. Experiment:  $\blacksquare$ , the present data. Theory: ---, the Olson formula for process (6); ----, the Olson formula for process (9); ----, the Olson formula for process (10); ----, the Olson formula for the accidental resonance case.



**Figure 8.** Charge-transfer cross sections for  $O^+$  ions in collisions with  $C_3H_8$  molecules. Experiment:  $\bullet$ , the present data. Theory: ---, the Olson formula for process (7); ----, the Olson formula for process (11); ----, the Olson formula for process (12); ----, the Olson formula for the accidental resonance case.

coincide well with the present data. This suggests that constant cross sections at energies below 0.8 keV can be due to the near resonance for process (8) accompanied by the vibrational excitation of the product target molecular ion, meanwhile process (5) accompanied by the

vibrational excitation ( $v_f \sim 5$ ) of the product target molecular ion becomes dominant above 0.8 keV.

# 3.5. $C_2H_6$ and $C_3H_8$ molecules

Figures 7 and 8 show the present experimental cross sections for  $O^+(^4S) + C_2H_6$  and  $C_3H_8$  collisions, respectively. Both results decrease slowly as the incident energy increases, but tend to level off around 1.2 keV, similar to  $O^+ + CH_4$  collisions (see figure 5).

In  $O^+ + C_2H_6$  collisions, the Olson formula has been used to calculate the cross sections under various collision conditions. The calculated results (chain curve) for the nearly resonant charge transfer process (9) are close to the present measurement at energies above 1.2 keV. Better agreement with experimental data has been obtained under the assumption that the incident  $O^+$  ions capture an electron into either the ground or the excited  $O^*(^1D)$  state, meanwhile the target molecular ion is vibrationally excited (full curve).

In  $O^+ + C_3H_8$  collisions, the calculated results (full curve) using the Olson formula reproduce the present results nicely, if the product target molecular ion is assumed to be in a vibrationally excited state, resulting in a full resonance process.

#### 4. Concluding remarks

We presented the cross sections for charge transfer by the ground state O<sup>+</sup>(<sup>4</sup>S) ions in collisions with H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> molecules in the energy range 0.2–4.5 keV. The observed cross sections show the gradual increase as the collision energy decreases for most of the present collision systems except for H<sub>2</sub>, CO and C<sub>2</sub>H<sub>2</sub>. This resonance feature for hydrocarbon molecules, which are the exothermic reactions, can be attributed to the process of charge transfer resulting in the vibrationally excited product molecular ions. Even for a  $C_2H_2$  target, it is expected that vibrationally excited states of product  $C_2H_2^+$  ions also play a key role in charge transfer. Although the O<sup>+</sup> + CO<sub>2</sub> collision is endothermic, accidental resonant charge transfer is expected to occur through thermally and vibrationally excited states of target molecules due to its small energy defect. While the cross sections for endothermic  $O^+ + CO$ collisions behave they increase as the collision energy increases. In fact, most of these features are confirmed by theoretical calculations using the Olson formula. It is noted that cross sections with the full resonance feature show a systematic relationship with the ionization energy of target molecules. We will discuss details of this point and the construction of an empirical scaling in the forthcoming paper. The present cross sections for H<sub>2</sub> molecules show a minimum at around 2 keV and increase as the collision energy decreases. This dependence, in particular below about 2 keV, should be studied both experimentally and theoretically.

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#### References

Bashkin S and Stoner J O Jr 1975 Atomic Energy Levels and Grotrian Diagrams vol I Hydrogen —Phosphorus xv (Amsterdam: North-Holland)

Dalgarno A 1990 *Molecular Processes in Space* ed T Watanabe, I Shimamura, M Shimizu and Y Itikawa (New York: Plenum) p 1

Flesch G D and Ng C Y 1991a J. Geophys. Res. 96 21 403

——1991b J. Chem. Phys. **94** 2372

Fuselier S A, Shelley E G, Goldstein B E, Goldstein R, Neugebauer M, Ip W-H, Balsiger H and Rème H 1991 Astrophys. J. 379 734

Gustaffson E and Lindholm E 1960 Ark. Fys. 18 219

Hoffman J M, Miller G H and Lockwood G L 1982 Phys. Rev. A 25 1930

Irvine A D and Latimer C J 1991 J. Phys. B: At. Mol. Opt. Phys. 24 L145

Janev R K 1995 Atomic and Molecular Processes in Fusion Edge Plasmas ed R K Janev (New York: Plenum) p 1 Kimura M and Lane N F 1989 Advances in Atomic, Molecular and Optical Physics vol 26, ed D R Bates and B Bederson

(New York: Academic) p 76 Kimura M, Li Y, Hirsch G and Buenker R J 1995 *Phys. Rev.* A **52** 1196

——1996 Phys. Rev. A 54 5019

Kusakabe T, Asahina K, Gu J P, Hirsch G, Buenker R J, Kimura M, Tawara H and Nakai Y 2000a *Phys. Rev.* A **62** 062714

Kusakabe T, Asahina K, Iida A, Tanaka Y, Li Y, Hirsch G, Buenker R J, Kimura M, Tawara H and Nakai Y 2000b Phys. Rev. A 62 062715

Kusakabe T, Horiuchi T, Nakai Y and Tawara H 1998 Japan. J. Appl. Phys. 37 369

Kusakabe T, Hosomi K, Nakanishi H, Nakai Y, Sasao M, Tawara H and Kimura M 1999 Phys. Rev. A 60 344

Kusakabe T, Imou K, Hosomi K, Nakanishi H, Satoh S, Tomita N, Kimura M, Nakai Y, Sasao M and Tawara H 2002 to be published

Kusakabe T, Mizumoto Y, Katsurayama K and Tawara H 1990b J. Phys. Soc. Japan 59 1987

Kusakabe T, Ohmiya M and Wada K 1993 Japan. J. Appl. Phys. 31 4093

Kusakabe T, Yoneda H, Mizumoto Y and Katsurayama K 1990a J. Phys. Soc. Japan 59 1218

Lide DR (ed) 1999 CRC Handbook of Chemistry and Physics 80th edn (Boca Raton, FL: Chemical Rubber Company)

Lindsay B G, Sieglaff D R, Smith K A and Stebbings R F 1999 J. Phys. B: At. Mol. Opt. Phys. 32 4697

Lisse C M et al 1996 Science 274 205

Lockwood G J, Miller G H and Hoffman J M 1978 Phys. Rev. A 18 935

Moran T F and Wilcox J B 1978 J. Chem. Phys. 69 1397

Nutt W L, McCullough R W and Gilbody H B 1979 J. Phys. B: At. Mol. Phys. 12 L157

Olson R E 1972 Phys. Rev. A 6 1822

Phaneuf R A, Meyer F W and McKnight R H 1978 Phys. Rev. A 17 534

Rutherford J A and Vroom D A 1976 J. Chem. Phys. 64 3057

Sieglaff D R, Lindsay B G, Smith K A and Stebbings R F 1999 Phys. Rev. A 59 3538

Xu Y, Thomas E W and Moran T F 1990 J. Phys. B: At. Mol. Opt. Phys. 23 1235