Apart from protons and alpha particles, the solar wind contains a small percentage of multiply charged C, O, N and Ne ions. In addition, very small fractions of intermediate charged Mg, Si, S and Fe ions are present in the solar wind (Schwadron and Cravens, 2000). The solar winds can be divided in slow and fast winds at approximately 200 – 400 km s\(^{-1}\) and approximately 500 – 1000 km s\(^{-1}\), respectively. The full velocity range encompassed by the slow and fast winds corresponds to a collision energy range of approximately 0.2 – 6 keV/amu.

The most abundant solar wind minor ion is O\(^{6+}\), which has not been considered in great detail because its emission falls just below the low-energy detection limits of *Chandra* and *XMM-Newton*. OVI emission has been detected in FUSE observations of comet C/WM1 (Weaver et al., 2002) and EUVE observations of comet Hyakutake (Krasnopolsky and Mumma, 2001). Oxygen ions precipitating into the Jovian atmosphere are important contributors to the observed EUV and X-ray emission of the aurorae of Jupiter (Waite et al., 1994). Model calculations based on O\(^{7+}\) – H\(_2\) interactions underline the important role of O\(^{6+}\) ions as line emitters (Kharchenko et al., 1998; Liu and Schultz, 1999).

In particular, state selective electron capture by O\(^{6+}\) in collisions on H, H\(_2\) and He has been studied extensively, e.g. refs. (Dijkkamp et al., 1985; Fritsch and Lin, 1986; Shimakura et al., 1987; Beijers et al., 1992; Liu and Schultz, 1999; Lubinski et al., 2000; Kearns et al., 2003). For many typical cometary and planetary target species such as CO, CO\(_2\) and H\(_2\)O the availability of experimental or theoretical data is very limited (Bodewits et al., 2004).

In this chapter we will focus on the one-electron capture in 0.1 – 7.5 keV/amu collisions of O\(^{6+}\) on H\(_2\)O molecules. Water molecules are the most likely electron donors in the interaction of the solar wind with comets.
Figure 6.1: Velocity dependence of charge exchange spectra for collisions between O\(^{6+}\) and H\(_2\)O. Shown are the first order (10 – 20 nm) and the second order (22 – 32 nm) spectra for collision energies of 7.5 keV/amu (top), 0.38 keV/amu (middle) and 0.11 keV/amu (bottom). The spectra are corrected for the accumulated charge and target pressure, but not for the spectrometer’s wavelength dependent response. Second order spectra are blown up for the ease of presentation.

6.1 Experiment

All experimental data in this chapter were obtained with the Photon Emission Spectroscopy (PES) experiment described in Chapter 4. Fig. 6.1 shows typical spectra obtained with the PES set up, at different collision velocities. With the 1200 grooves/mm grating used for this experiment, the resolution of the spectrometer is approximately 0.3 nm FWHM. Spectra were measured at two different positions along the Rowland circle, in order to obtain first and second order spectra. In second order, the spectrometer is less sensitive, but the 1s\(^2\) 4d–1s\(^2\) 2p and 1s\(^2\) 4s–1s\(^2\) 2p peaks that overlay in first order are clearly separated.
6.2 Spectral Analysis

All spectra were analyzed by fitting Gaussian peaks to the data. Emission cross sections were deduced from photon yields by using the following relation:

$$\sigma_{em} = A \cdot S(\lambda) \frac{q}{Q} N$$

(6.1)

where $S(\lambda)$ is the spectrometer's wavelength dependent response, $q$ is the charge state of the incoming ion, $Q$ is the accumulated charge over which is integrated, $N$ is the photon yield. $A$ includes all parameters that are kept constant during our experiments, amongst which the target density, and is found by calibration via known cross sections for He$^{2+}$+H$_2$O (Seredyuk et al., 2005a; Bodewits et al., 2005, 2006). The resulting emission cross sections are given in Table 6.1.

To derive population cross sections, the measured emission cross sections should be corrected for branching ratios and cascade effects. The decay scheme of OVI is given in Fig. 6.2. Transitions from $n = 4 \rightarrow 3$ fall outside the wavelength range accessible to the spectrometer when equipped with the 1200 G/mm grating used here. Transitions from $n=5 \rightarrow 2$ fall within the observable wavelength regime, but lie too close to the strong 4p–2s transition to be resolved in first order. In second order however, the separation between the lines becomes large enough for individual detection and careful inspection of these spectra shows a very weak emission feature due to the 5s,5d – 2p transitions at $\sim$23.4 nm (see Fig. 6.1). We will therefore assume that capture into $n = 5$ is negligible. The population cross sections can therefore be derived from the measured line emission cross sections by means of the following relations:

<table>
<thead>
<tr>
<th>E (keV/amu)</th>
<th>11.6 nm</th>
<th>13.0 nm</th>
<th>13.2 nm</th>
<th>15.0 nm</th>
<th>17.3 nm</th>
<th>18.4 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.11 ........</td>
<td>11 ± 1.1</td>
<td>3.2 ± 0.3</td>
<td>5.4 ± 0.5</td>
<td>4.2 ± 0.4</td>
<td>5 ± 0.5</td>
<td>2.6 ± 0.3</td>
</tr>
<tr>
<td>0.19 ........</td>
<td>8.7 ± 0.9</td>
<td>3.2 ± 0.3</td>
<td>5.3 ± 0.5</td>
<td>4.4 ± 0.4</td>
<td>8 ± 0.8</td>
<td>2.1 ± 0.2</td>
</tr>
<tr>
<td>0.38 ........</td>
<td>7.3 ± 0.7</td>
<td>2.8 ± 0.3</td>
<td>5.3 ± 0.5</td>
<td>4.2 ± 0.4</td>
<td>10 ± 1.0</td>
<td>1.7 ± 0.2</td>
</tr>
<tr>
<td>1.31 ........</td>
<td>5.0 ± 0.5</td>
<td>3.0 ± 0.3</td>
<td>4.1 ± 0.4</td>
<td>3.1 ± 0.3</td>
<td>12 ± 1.2</td>
<td>1.2 ± 0.1</td>
</tr>
<tr>
<td>3.94 ........</td>
<td>4.3 ± 0.4</td>
<td>4.5 ± 0.5</td>
<td>2.9 ± 0.3</td>
<td>3.6 ± 0.4</td>
<td>22 ± 2.2</td>
<td>1.3 ± 0.1</td>
</tr>
<tr>
<td>7.50 ........</td>
<td>3.3 ± 0.3</td>
<td>4.7 ± 0.5</td>
<td>1.4 ± 0.1</td>
<td>3.2 ± 0.3</td>
<td>33 ± 3.3</td>
<td>1.3 ± 0.1</td>
</tr>
</tbody>
</table>

Table 6.1: Fit results - measured emission cross sections for one electron capture in O$^{6+}$+H$_2$O collisions, for different collision energies. All cross sections are in units of $10^{-16}$ cm$^2$. Only relative errors are given. The systematic uncertainty is approximately 25%.
Electron Capture Channels in Collisions between O$^{6+}$ and H$_2$O

Figure 6.2: Grotrian diagram of OVI (1s$^2$ n$\ell$) transitions. Observed transitions are indicated with solid lines, other transitions by dashed lines. Wavelengths are given in nanometers, the numbers between brackets are the branching ratios.

\[
\begin{align*}
\sigma(4s) &= \sigma_{en}(13.2)/0.59 \\
\sigma(4p) &= \sigma_{en}(11.6)/0.77 \\
\sigma(4d) &= \sigma_{en}(13.0)/0.77 \\
\sigma(3s) &= \sigma_{en}(18.4) - 0.19\sigma(4p) \\
&= \sigma_{en}(18.4) - 0.25\sigma_{en}(11.6) \\
\sigma(3p) &= \sigma_{en}(15.0) - 0.41\sigma(4s) - 0.23\sigma(4d) \\
&= \sigma_{en}(15.0) - 0.69\sigma_{en}(13.2) - 0.30\sigma_{en}(13.0) \\
\sigma(3d + 4f) &= \sigma(17.3) - 0.04\sigma(4p) \\
&= \sigma(17.3) - 0.03\sigma_{en}(11.6)
\end{align*}
\]

From these relations, it is clear that except for the 4f state, capture into the $n = 4$ states is observed directly, and that population cross sections for $n = 3$ are derived indirectly from the line emission cross sections. It is not possible to separate capture into the 1s$^2$3d and 1s$^2$4f states without observing the direct transition between those two states at longer wavelengths.

Assuming that one electron capture populates only $n = 3, 4$ states, the total one electron capture cross sections can be found by adding up these state selective cross sections:

\[
\sigma_i = \sum_{n\ell} \sigma(n\ell)
\]
The results are subject to a number of uncertainties. The dominating absolute uncertainty is that arising from the spectrometer’s calibration by means of cross sections for CXE from He$^{2+}$ ions, and is approximately 20% (Bodewits et al., 2006). This error affects all data points, and leads to a simple scaling factor. A more complex error is due to the uncertainty in the wavelength dependent sensitivity of the spectrometer, which we estimate to be 10 – 15%. Added in quadrature these uncertainties lead to an absolute systematic uncertainty of 25%. The uncertainty associated with the wavelength-dependent sensitivity may also influence the relative line strengths which are of importance when assessing cascade contributions. Target fluctuations were controlled by performing regular calibration measurements, but lead to a random error in the order of 5%. Statistical errors for these experiments were small due to high photon yields and never exceeded 1% (1σ). Therefore we assume a relative uncertainty of 10% in the line emission cross sections.

### 6.3 Results and Discussion

#### 6.3.1 Population Cross Sections

The state selective cross sections, determined from the line emission data via equation 6.2, are shown in Fig. 6.3. Cross sections for electron capture into the 1s$^2$3s and 1s$^2$3p states are very small ($\leq 10^{-16} \text{ cm}^2$). Therefore, although we did not measure separate 1s$^2$4f and 1s$^2$3d cross sections, it seems very reasonable to assume that capture into 1s$^2$3d is not significant and thus, that $n = 4$ is the dominant reaction channel in collisions between O$^{6+}$ and H$_2$O molecules, as expected from the Classical-over-the-Barrier model (Fig. 6.5), and in line with the TES experiments by Seredyuk et al. (2005c).

At low energies, the 1s$^2$4p–1s$^2$2s transition at 11.6 nm is the strongest line in the spectrum, followed by the relatively strong 1s$^2$4s–1s$^2$2p emission. Around 0.5 keV/amu, all emission lines in the spectrum are roughly equally strong, as are the capture cross sections. At high velocity, the spectrum is completely dominated by the 1s$^2$3d–1s$^2$2p transition at 17.3 nm as the $\ell$-state distribution has shifted to higher states.

The population of low $\ell$-states at low energy, and a near statistical distribution at higher energy is a general feature in electron capture by multiply charged ions (see e.g. Janev and Winter, 1985; Lubinski et al., 2001). To illustrate the change in the $\ell$-distribution more

<table>
<thead>
<tr>
<th>E (keV/amu)</th>
<th>3s</th>
<th>3p</th>
<th>4s</th>
<th>4p</th>
<th>4d</th>
<th>4f + 3d</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.11</td>
<td>0.8 ± 0.3</td>
<td>-0.5 ± 0.6</td>
<td>9.1 ± 0.9</td>
<td>14 ± 1.4</td>
<td>4.1 ± 0.4</td>
<td>4.8 ± 0.6</td>
<td>33 ± 1.9</td>
</tr>
<tr>
<td>0.19</td>
<td>0.4 ± 0.3</td>
<td>-0.2 ± 0.6</td>
<td>9.0 ± 0.9</td>
<td>11 ± 1.1</td>
<td>4.1 ± 0.4</td>
<td>7.6 ± 0.8</td>
<td>32 ± 1.8</td>
</tr>
<tr>
<td>0.38</td>
<td>0.0 ± 0.2</td>
<td>-0.3 ± 0.6</td>
<td>8.9 ± 0.9</td>
<td>9.5 ± 1.0</td>
<td>3.6 ± 0.4</td>
<td>9.4 ± 1.0</td>
<td>31 ± 1.8</td>
</tr>
<tr>
<td>1.31</td>
<td>-0.2 ± 0.2</td>
<td>-0.6 ± 0.4</td>
<td>7.0 ± 0.7</td>
<td>6.5 ± 0.7</td>
<td>3.9 ± 0.4</td>
<td>11 ± 1.2</td>
<td>28 ± 1.6</td>
</tr>
<tr>
<td>3.94</td>
<td>0.3 ± 0.2</td>
<td>0.2 ± 0.4</td>
<td>5.0 ± 0.5</td>
<td>5.5 ± 0.6</td>
<td>5.8 ± 0.6</td>
<td>22 ± 2.2</td>
<td>39 ± 2.4</td>
</tr>
<tr>
<td>7.50</td>
<td>0.9 ± 0.1</td>
<td>0.9 ± 0.4</td>
<td>2.3 ± 0.2</td>
<td>4.3 ± 0.4</td>
<td>6.1 ± 0.6</td>
<td>33 ± 3.3</td>
<td>47 ± 3.4</td>
</tr>
</tbody>
</table>
Figure 6.3: Velocity dependence of state selective, single electron capture cross sections for O$^{6+}$ + H$_2$O. **Upper panel:** Capture into $n = 4$. □ - $\sigma(4s)$; • - $\sigma(4p)$; △ - $\sigma(4d)$; ▼ - $\sigma(3d + 4f)$. **Lower panel:** Capture into $n = 3$. • - $\sigma(3s)$; □ - $\sigma(3p)$. Lines are drawn to guide the eye. Only relative errors are given. The systematic uncertainty is approximately 25%.
6.3 Results and Discussion

Figure 6.4: Comparison of measured (grey) and theoretical distribution (black) over the $4\ell$-states. **Left panel:** Measured distribution at 0.11 keV/amu, compared with a radial coupling determined low energy distribution (Abramov et al., 1978; Janev et al., 1983). **Right panel:** Measured distribution at 7.5 keV/amu, compared with a statistical $\ell$-distribution typical for higher collision velocities.

Figure 6.5: Over-the-Barrier predictions for one electron capture in $O^{6+} + H_2O$ collisions. **Left panel:** Reaction windows for collision energies of 0.25 and 4 keV/amu. $OVI$ states are indicated. **Right panel:** Collision energy dependence of the maximum none-integer angular momentum (see text).

Qualitatively, two measured fractional population of the $4\ell$-states are shown in Fig. 6.4. At the lowest velocity, there is a fair agreement with the distribution function predicted for electron transfer via purely radial coupling (Abramov et al., 1978; Janev et al., 1983). At the highest velocity, where rotational couplings are important, the $\ell$-state distribution roughly resembles a statistical distribution ($2\ell + 1$), but the 4f state seems to be overpopulated with respect to the other $4\ell$ states.

To some extent, as rotational coupling is linked to the collisional angular momentum, the shift in the $\ell$-state distribution over angular momenta may be understood in terms of the classical Over-the-Barrier model (Burgdörfer et al., 1986). In the frame of the $O^{5+}$ ion,
Table 6.3: Ionization potentials and resulting Over-the-Barrier predictions for capture distances and geometrical cross sections.

<table>
<thead>
<tr>
<th>#</th>
<th>( \text{IP}_n ) (eV)</th>
<th>( R_{c,n} ) (a.u.)</th>
<th>( \sigma_n ) (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.6</td>
<td>12.7</td>
<td>39</td>
</tr>
<tr>
<td>2</td>
<td>27</td>
<td>8.6</td>
<td>11</td>
</tr>
<tr>
<td>3</td>
<td>(<del>45</del>)</td>
<td>6.9</td>
<td>21</td>
</tr>
</tbody>
</table>

the target has an apparent angular momentum \( L \) of the order \( L = bv_p \), with \( b \) the impact parameter and \( v_p \) the projectile velocity. The maximum impact parameter is the capture radius \( R_c \) at which the electron can cross the potential barrier between the target and projectile (Chapter 3). The maximum (non-integer) angular momentum \( \ell \) of the captured electron can then be estimated using the relation:

\[
L^2 = \ell (\ell + 1)
\]  

(6.4)

In figure 6.5, the maximum angular momentum for \( \text{O}^{6+} + \text{H}_2\text{O} \) collisions is given as a function of collision energy. Capture into \( \ell = 3 \) becomes possible at collision energies above 2 keV/amu, above which we indeed observe a steep increase in the 4f capture cross section (Fig. 6.3).

As the 4f population is determined from the 1s\(^2\)3d–1s\(^2\)2p transition, the apparent overpopulation of the 4f state at both low and high collision energies might be partly due to capture into the 3d and 5g states. As mentioned before, the measured 3s and 3p capture cross sections are close to zero and therefore it seems logic that capture is also negligible. However, in their TES experiments (0.75 – 1.5 keV/amu) Seredyuk et al. (2005c) find that next to dominant capture into \( n = 4 \), formation of \( \text{O}^{5+}(n = 3) \) through dissociative capture channels is significant (up to 50%). Capture via these channels might therefore explain the apparent slight overpopulation of the 4f state at low energies. However, the contribution of these dissociative channels becomes smaller with decreasing velocity (Seredyuk et al., 2005c). At higher velocities, the reaction window widens enough to allow capture into \( n = 5 \) (Fig. 6.5). Also, the higher velocities result in higher maximum values of the electron’s angular momentum. The apparent overpopulation of 4f can therefore be attributed to cascade contributions of the 5g state.

6.3.2 Total Cross Sections

We also used our data to determine velocity dependent, total one electron capture cross sections. The results are shown in Fig. 6.6. Above 1 keV/amu, where capture into 1s\(^2\)4f becomes more and more important, the total cross section increases strongly with velocity. In the figure, total one electron capture cross sections for collisions with H and H\(_2\) are also given for comparison. According to the classical-over-the-barrier (CoB) model, one electron capture cross sections scale with the inverse of the ionization potential of the target (Chapter 3). The binding energy of water is 12.6 eV, that of H is 13.6 eV and that of
6.3 Results and Discussion

Figure 6.6: Velocity dependence of total one electron capture cross sections for collisions between O$^{6+}$ and H$_2$O – •, compared with charge exchange cross sections for H$_2$ (△ – Dijkkamp et al. (1985), ▽ – Lubinski et al. (2000)) and H (□ – Dijkkamp et al. (1985)). ○ – total charge changing cross section from Mawhorter et al. (2007). ▲ – total charge changing cross section for C$^{6+}$+H$_2$O (Greenwood et al., 2001). Lines are drawn to guide the eye. Only relative errors are given. The systematic uncertainty is approximately 25%.

H$_2$ is 16.1 eV. The CoB model thus predicts that the one electron capture cross sections for all species will be comparable, which is confirmed by our results.

Total charge changing cross sections for O$^{6+}$+H$_2$O have recently been measured by Mawhorter et al. (2007). At a collision energy of 2.6 keV/amu, they measured a charge changing (O$^{6+}$ → O$^{5+}$) cross section of $(53 \pm 4) \times 10^{-16}$ cm$^2$. A similar cross section has been measured for C$^{6+}$+H$_2$O collisions (Greenwood et al., 2001). These cross sections are much larger than the one electron capture cross sections determined by us at comparable energies, which by interpolation would be approximately $(34 \pm 8) \times 10^{-16}$ cm$^2$. The difference can only be explained by auto-ionizing double electron capture processes.

The Over-the-Barrier model (Niehaus, 1986) can be used to make an estimation of the multiple electron capture cross sections. Using binding energies from literature (Alvarado et al., 2005) and assuming the binding energy of the third electron to be approximately 45 eV, we find cross sections of $\sigma_1 = 39$, $\sigma_2 = 11$ and $\sigma_3 = 21 \times 10^{-16}$ cm$^2$ (see Table 6.3). The $\sigma_1$ agrees well with the single electron capture cross section we measured, while the sum of $\sigma_1$ and $\sigma_2$ is close to the aforementioned charge changing cross sections ($q = 6 \rightarrow q = 5$).

Following the argumentation of Knoop et al. (2006), it is estimated that two electron
capture will mainly populate \((3\ell n' \ell', n' = 5 – 7)\) configurations. The resulting energy defects would coincide with the feature observed in the TES spectra at energy defects of 20 – 30 eV (Seredyuk et al., 2005c).

This implies that the cross sections for double charge exchange \((\text{O}^6+ \rightarrow \text{O}^4+)\) measured by Mawhorter et al. (2007) should be largely attributed to auto-ionizing 3 electron capture reactions, rather than bound double electron capture reactions.

### 6.4 Conclusions

In the interaction between comets and the solar wind, collisions between the \(\text{O}^6+\) and water play a key role. In this section, we have presented velocity dependent state selective and total one electron capture cross sections for collisions between \(\text{O}^6+\) and \(\text{H}_2\text{O}\), at collision energies between 0.11 – 7.5 keV/amu. These energies correspond to velocities typical for the solar wind, i.e. 150 – 1200 km s\(^{-1}\).

Our results show that single electron capture mainly leads to population of the \(n = 4\) state and that the subsequent decay gives rise to strong EUV emission between 10 – 20 nm. The relative strength of the different EUV lines strongly depends on the collision velocity and might be used as a velocimetric diagnostic in comet-wind interactions, for example by observing the ratio between the \(1s^23d–1s^22p\) and \(1s^24p–1s^22s\) transitions.

We also used our data to determine total one electron capture cross sections. From a comparison with other experimental studies, we conclude that direct one electron capture cross section constitutes only 60% of the total charge changing cross section, and that multiple electron processes thus play an important role in collisions between \(\text{O}^6+\) and \(\text{H}_2\text{O}\). These results emphasize that a thorough understanding of charge exchange processes is of utmost importance for modeling of solar wind charge state distributions in cometary and planetary atmospheres.