Molecular dissociation induced by electron transfer to multicharged ions
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Document Version
Publisher's PDF, also known as Version of record

Publication date:
1996

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
Folkerts, H. O. (1996). Molecular dissociation induced by electron transfer to multicharged ions s.n.

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Chapter 5

Dissociation of CO induced by electron transfer to He$^{2+}$ ions

The dissociation of multicharged CO$^q^+$ ions ($q \leq 3$) produced in collisions with 4 keV/amu He$^{2+}$ has been studied by time-of-flight and coincidence time-difference measurements. We have developed a method to transform the time-of-flight and time-difference spectra into total-kinetic-energy distributions. From these distributions we have determined various contributions associated with different dissociation channels. We have found that almost all the CO$^+$ ions are produced in one of the stable states, which can be understood in the framework of the overbarrier model. Our results for the production and the dissociation of CO$^{2+}$ and CO$^{3+}$ are compared to the results of photoionisation and fast heavy ion collisions. From this comparison we found that keV He$^{2+}$ collisions lead to the population of lower excited states than collisions with MeV Ar$^{14+}$. The ratio between CO$^{3+}$ and CO$^{2+}$ transient ion production is found to be much larger than reported for photoionisation, while the kinetic energy distributions are comparable.
5.1 Introduction

Ionisation and subsequent dissociation of carbon monoxide molecules has been studied over the last decades by various experimental methods. Electron impact [66-68], intense laser fields [69,70] and photoionisation [71,72] have been used to study the formation of CO$^+$ and CO$^{2+}$ ions and fragments originating from CO$q^+$ with $q \leq 3$. With various experimental techniques the thresholds for molecular ion and ion-pair formation have been determined as well as the kinetic energies and the relative intensities of the fragments. Dissociation of more highly charged molecular ions has been studied using fast highly charged heavy ions [73-75]. As reported by Sampoll et al. [73] collisions with 96 MeV Ar$^{14+}$ projectiles lead, on average, to higher excited states than photoionisation [72].

It is well established that also low energy highly charged ions very efficiently lead to multiple ionisation of target atoms. This is due to the relatively small binding energy of the target electrons compared to the potential energy of the highly charged ion together with the fact that electrons are captured nearly resonantly. Multiple ionisation is also observed in keV collisions with molecular targets as reported by Werner et al. [76,77], Beckord et al. [78] and Remscheid et al. [79]. Due to the relative large impact parameters at which electron capture takes place, these low energy collisions are assumed to be more "gentle" than collisions with fast heavy ions and therefore expected to lead to lower excited states.

Dissociation of molecules in ion-molecule collisions is assumed to proceed in a two step process [14]. The first step is the direct interaction between the projectile and the electrons of the molecule leading to excitation, ionisation and electron capture by the projectile:

$$\text{He}^{2+} + \text{CO} \rightarrow \text{He}^{(2-r)+} + \text{CO}^{(r+s)+} + \text{e}^- \quad (5.1)$$

with $r \leq 2$. These processes are assumed to take place in a time which is much shorter than the molecular vibration time and thus occur at fixed internuclear distance (section 5.4.1). Therefore the Franck-Condon principle is applicable which means that we can describe an electronic transition as a vertical transition in the potential energy diagram.

The second step is the decay of these (excited) molecular ions by dissociation into fragments:

$$\text{CO}^{q+} \rightarrow C^t + O^{(q-t)+} + U_{KER} \quad (5.2)$$

where $U_{KER}$ is the kinetic energy released in the dissociation and $0 \leq t \leq q$. The dissociation channels depend on the potential energy of the intermediate dissociative state and are influenced by the interaction with neighbouring states (potential energy curve crossings). A certain charge state of the molecular ion can lead to various charge states of the fragments with various amounts of kinetic energy.

In this chapter we present a study of CO dissociation induced by collisions with 4 keV/amu He$^{2+}$. With time-of-flight and coincidence time-difference measurements we have determined relative abundances of the various dissociation chan-
nels and the kinetic energy released in the dissociation. From these quantities we obtain information on the excited states populated in the transient molecular ion. For this collision system total cross sections for molecular and fragment-ion formation and non-dissociative and dissociative electron capture have been measured by Graham et al. [80] and Shah et al. [81] at the same collision energy. Kinetic energy distributions associated with the various dissociation channels are reported here for the first time.

5.2 Experiment

In the experiments presented here a continuous beam of He\(^{2+}\) ions is extracted from the ECR ion source at 4 to 8 kV. With a chopper the ion beam can be pulsed with a frequency of 25 kHz in pulses of about 20 ns. The ion beam is impinged on a gaseous CO molecular target which has a full width at half maximum of 3 mm (see chapter 2). The resulting molecular ions and charged fragments are extracted perpendicular to the ion beam into a so called reflectron mass spectrometer. Their charge/mass ratio is determined by measuring their time-of-flight (TOF) from the scattering centre to the detector, i.e. the time interval between beam pulse and detector signal. The design of the reflectron is based on the work of Mamyrin et al. [22] and is described in more detail in section 2.3.2. In the detector the ions travel in a field free region towards an electrostatic mirror in which their trajectories are reversed back into the field free region towards multichannel plates used for detection. With appropriate adjustment of the parameters of the reflecting system energy differences due to different starting positions in the extraction field are compensated regarding the total time-of-flight to second order. This mirror technique together with a long drift length results in a high mass resolution (section 5.3.1).

The initial kinetic energy of the fragments caused by the dissociation results in a broadening of the peaks in the TOF spectra. Ions with their initial velocity towards the spectrometer have a shorter flight time than the ones with the initial velocity in the opposite direction since the latter ones first have to be turned around in the electric field before they can reach the spectrometer aperture. For low extraction fields and sufficient high kinetic energy even a splitting into two peaks occurs since fragments ejected along the beam axis will be intercepted by the entrance diaphragm of the spectrometer and will therefore not be detected. From the time-of-flight differences between those peaks one can calculate the total kinetic energy released in the dissociation, as is discussed in section 2.3.3.

By using a pulsed beam, we have measured singles time-of-flight spectra. From the time interval between beam pulse and detector signal we can identify the reaction products. To calibrate the spectrometer and to determine the mass-resolution we have performed measurements with atomic targets like argon and krypton. Using a high extraction voltage we have determined the relative cross sections for ion formation in He\(^{2+}\) on CO collisions. Measurements at low extraction voltage are performed to determine the kinetic energy release. During the measurements the target pressure was about 8 mPa and the intensity of the
chopped beam was in the order of 100 pA.

Additional information is obtained from coincidence time-difference measurements. Here the start is given by the first arriving ion and the stop by the second. In this way only $C_9^{+} + O_7^{+}$ ion pairs are detected. From these spectra we have obtained direct information on the charge distribution and we have determined the kinetic energy distributions associated with the ion pairs. For a better signal to noise ratio these measurements are performed with a very low target pressure of around 0.4 mPa and a beam intensity of about 100 pA. The background pressure was about 0.02 mPa. The total count rate was around 400 sec⁻¹.

5.3 Experimental results

5.3.1 High extraction voltage

For calibration of the spectrometer we have measured the time-of-flight of the differently charged argon ions after charge exchange with 4.66 keV/amu $C_6^{6+}$ projectiles. The TOF spectrum is shown in figure 5.1a. Sharp $Ar_q^{q+}$ peaks are observed up to $q=8$. The $H^+$ peak is due to residual water vapour in the vacuum system. The production of $Ar_7^{7+}$ and $Ar_8^{8+}$ in a collision with a sixfold charged particle is an intriguing observation which is discussed in an article by de Nijs et al. [82]. Figure 5.1b shows the linearity of the time-of-flight versus the square root of the mass to charge ratio.

To determine the mass resolution we have measured a TOF spectrum of singly charged krypton isotopes which is shown in figure 5.2. A high reso-
Dissociation of CO induced by electron transfer to He$^{2+}$ ions

A high extraction voltage of 350 V/cm is used to minimise the broadening due to the recoil energy. The Kr$^+$ ions are produced in collisions with 4 keV/amu He$^{2+}$ projectiles. The diaphragm at the entrance of the spectrometer was 6 mm. The spectrum reproduces the different isotopes according to their natural abundances. Since the time of flight is proportional to the square root of the mass, the mass resolution is given by:

$$\frac{m}{\Delta m} = \frac{t^2}{(t + \Delta t)^2 - t^2} \approx \frac{t}{2\Delta t}. \quad (5.3)$$

From figure 5.2 we determine a FWHM of 34 ns which corresponds to a resolution of $m/\Delta m = 420$.

There are four main contributions to the width of the peaks.

(i) The width of a beam pulse. This can be calculated from the dimensions of the chopper and its position in the beam line. For a 4 keV/amu He$^{2+}$ we found that the pulse width is around 15 ns.

(ii) The crossing time of a beam pulse through the target. For a target with a FWHM of 3.0 ± 0.5 mm this is 5 ns.

(iii) Different starting positions in the extraction field. Although time differences due to this effect are compensated to second order by the reflectron there is still a small broadening effect which is ≤ 10 ns. To compare, without the time focusing of the reflectron a difference in starting position of 1.5 mm would lead to a time spread of 300 ns.

(iv) The initial kinetic energy of the krypton ions. Due to the mass difference of the projectile and the target the recoil energy of the krypton is very low, in the order of 20 meV. There is also a thermal energy of about 10 meV. In an extraction field of 350 V/cm this gives a contribution to the peak width of 25 ns.

We assume that all other effects like broadening due to different trajectories in the spectrometer and differences in the pulse registration are smaller than 5 ns. So we can calculate the FWHM by summing the different contribution squared, giving $\Delta t \approx 31$ ns which is in agreement with the measured value of approximately 34 ns.

Figure 5.3 shows a time-of-flight spectrum resulting from collisions of 2 keV/amu He$^{2+}$ on CO molecules. This spectrum is measured with an...
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Figure 5.3: TOF spectrum of ions produced in 2 keV/amu He\(^{2+}\)/amu CO collisions measured with a high extraction field of 200 V/cm and a diaphragm of 8 mm.

Table 5.1: Relative yields normalised to 100% for ion formation in 2 keV/amu He\(^{2+}\)/amu CO collisions compared with the work of Graham et al. [14] (Ref.).

<table>
<thead>
<tr>
<th>Ion</th>
<th>This work</th>
<th>corrected</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(^{+})</td>
<td>29.9</td>
<td>23</td>
<td>25.8</td>
</tr>
<tr>
<td>CO(^{2+})</td>
<td>1.3</td>
<td>1</td>
<td>1.2</td>
</tr>
<tr>
<td>O(^{+})</td>
<td>30.6</td>
<td>32</td>
<td>32.3</td>
</tr>
<tr>
<td>C(^{+})</td>
<td>23.6</td>
<td>30</td>
<td>27.1</td>
</tr>
<tr>
<td>O(^{2+})</td>
<td>4.7</td>
<td>4.5</td>
<td>5.2</td>
</tr>
<tr>
<td>C(^{2+})</td>
<td>9.9</td>
<td>9.7</td>
<td>8.4</td>
</tr>
<tr>
<td>O(^{3+})</td>
<td>0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(^{3+})</td>
<td>0.14</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

However, from transmission calculations as described in section 2.3.3 we found that for the high energy fragments a correction is necessary, up to a factor of 3.8 for 16 eV C\(^{+}\) fragments. This correction can only be implemented if the energy distribution of the particles is known. When we assume energy distributions like the ones found for 4 keV/amu He\(^{2+}\)/amu CO as described in the next section, we can apply a correction to the measured values. The corrected cross sections are also listed in table 5.1. We see that the correction mainly influences the C\(^{+}\) ion formation cross section.

For collision systems where the product ions have low kinetic energy (e.g., collisions with atomic targets) such a correction is not necessary under these conditions.
5.3.2 Low extraction voltage

As described in section 2.3, information on kinetic energy release during fragmentation can be obtained by lowering the extraction voltage. In figure 5.4 a TOF spectrum is shown resulting from collisions of 4 keV/amu He\(^{2+}\) on CO measured with an extraction field of 50 V/cm and a diaphragm of 2 mm. The molecular ion peaks are still well defined, while the initial kinetic energy of the fragments clearly leads to a double peak structure. The two peaks on the right side of the CO\(^+\) peak are contributions of the isotopes \(^{13}\)CO and C\(^{18}\)O in the natural abundances of 1% and 0.2% respectively. The small contribution at 13 µs corresponds to a m/q value of 18, which is H\(_2\)O\(^+\) and \(^{18}\)O\(^+\).

In the middle of the C\(^+\) peak structure there is a clear peak due to a low kinetic energy contribution. Since this peak is not seen in the O\(^+\) structure, we can directly conclude that this is a result of the dissociation of CO\(^+\) into a C\(^+\) ion and a neutral O. From the width of the peak the kinetic energy release is calculated to be in the order of 1 eV. The other peaks are due to more energetic dissociation processes. In this part of the singles spectra it is not possible to distinguish between contributions from higher excited CO\(^+\) and low excited CO\(^{2+}\) states (see section 5.3.3).

From the peak structures we have determined the kinetic energy release as discussed in chapter 2. In this procedure all fragment ions are treated separately. For each fragment we have determined the exact time-of-flight (t\(_0\)) of the ion with no initial kinetic energy from the flight times of CO\(^+\) and CO\(^+\) and the \(\sqrt{m/q}\) dependence of the TOF.

Figure 5.4: TOF spectrum of ions produced in 4 keV/amu He\(^{2+}\) CO collisions measured with a low extraction field of 50 V/cm and a diaphragm of 2 mm.

This t\(_0\) marks the middle of the peak structure. The peak on the left side of t\(_0\) is the result of forward emitted fragments, while the peak at longer flight times is due to fragments emitted in the backward direction. In figure 5.5a and 5.5b both peaks are shown with on the x axis the time difference (ΔT/2) with respect to t\(_0\). The spectrum of the forward emitted ions contains much more counts than the other one, because of the higher transmission of the forward component. Also the shapes of these raw spectra are different due to the different transmission functions.

For both spectra we have transformed ΔT to KER, leading to two KER spectra. To correct these spectra for the energy dependent transmission we have multiplied them with the correspond-
Figure 5.5: \( \text{O}^+ \) fragments from the dissociation of CO molecular ions. a) and b) show the forward and backward emitted ions, respectively; full curve, counts versus \( \Delta T/2 \) (see text). Statistical errors are indicated by the broken curves. The corrected KER spectra are shown in figure c) and d) (full curves). The errors (broken curves) are the sum of statistical errors and the errors introduced by the correction.

The corrected spectra for all forward emitted fragments are shown in figure 5.6. The broken curves are the different components we can distinguish which are determined by a fit procedure. The fitting process is a free fit except for some restrictions i.e.: The functions are Gaussians of which the width increases with increasing energy. The number of Gaussians is chosen in such a way that when an extra Gauss is added this will largely
coincide with another contribution. In the O$^{2+}$ fit there is a Gauss locked around 17 eV because this corresponds to a distinct contribution of the C$^+$ spectrum.

Figure 5.6: Corrected KER spectra for all emitted charged fragments. a) C$^+$, b) C$^{2+}$, c) O$^+$, d) O$^{2+}$.

A Gauss curve does probably not exactly reflect the kinetic energy distribution of fragments from a certain process. For dissociation via a repulsive state the energy distribution is predicted to be a bit asymmetric with a high energy tail. In this prediction it is assumed that the ground state population is reflected in the shapes of the energy spectra produced by Franck-Condon excitation and subsequent dissociation of the repulsive states. This is discussed by Wood et al. [83] for dissociative ionisation of H$_2$. The population of the excited states of CO after He$^{2+}$ impact is not known and is just one of the goals of this study. Therefore the exact shape is unknown and we have used Gauss functions as an approximation.

From the fitted contributions we have determined relative cross sections for the production of the energetic fragments we can distinguish. Furthermore, since every C fragment is produced together with an O, we can combine the ion formation cross sections to estimate the relative cross sections for the various dissociation processes. If we only use the TOF data there is not a unambiguous solution. However, with the additional information from the coincidence measurements we are able to determine the weights of the different processes rather dependably. With the ratios between the different processes as listed in table 5.2, the related ion production cross sections are within 8% consistent with all single ion yields we have measured. A comparison between the results from the TOF spectra and the ones from the time-difference spectra is discussed in the next section.

### 5.3.3 Time-difference spectra

From chapter 2 (figure 2.10) we know that for an extraction voltage of 50 V/cm and a diaphragm of 2 mm the transmission for the backward emitted fragments is very low. This is no problem for the analysis of the singles spectra, since we have focused on the forward emitted ions which have the better statistics. For the coincidence time-
Table 5.2: **Relative cross sections for the various ionisation and dissociation processes in 4 keV/amu He$^{3+}$ on CO collisions determined from the singles TOF spectra.**

<table>
<thead>
<tr>
<th>Products</th>
<th>KER (eV)</th>
<th>FWHM (eV)</th>
<th>Rel. Xsec</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$^+$</td>
<td></td>
<td></td>
<td>52.4</td>
</tr>
<tr>
<td>CO$^2+$</td>
<td></td>
<td></td>
<td>1.3</td>
</tr>
<tr>
<td>C + O$^+$</td>
<td>1.5</td>
<td></td>
<td>0.2</td>
</tr>
<tr>
<td>C$^+$ + O</td>
<td>1.5</td>
<td></td>
<td>1.5</td>
</tr>
<tr>
<td>C$^{++}$ + O$^+$</td>
<td>7.5</td>
<td>7</td>
<td>7.4</td>
</tr>
<tr>
<td>C$^{++}$ + O$^+$</td>
<td>17</td>
<td>12</td>
<td>14.5</td>
</tr>
<tr>
<td>C$^{++}$ + O$^+$</td>
<td>28</td>
<td>16</td>
<td>3.9</td>
</tr>
<tr>
<td>C$^{++}$ + O$^{2+}$</td>
<td>9</td>
<td>8</td>
<td>0.6</td>
</tr>
<tr>
<td>C$^{2+}$ + O</td>
<td>9</td>
<td>8</td>
<td>1.1</td>
</tr>
<tr>
<td>C$^{2+}$ + O$^{2+}$</td>
<td>18</td>
<td>13</td>
<td>0.6</td>
</tr>
<tr>
<td>C$^{2+}$ + O$^{2+}$</td>
<td>31</td>
<td>19</td>
<td>3.1</td>
</tr>
<tr>
<td>C$^{2+}$ + O$^{2+}$</td>
<td>50</td>
<td>27</td>
<td>1.3</td>
</tr>
<tr>
<td>C$^{2+}$ + O$^{+}$</td>
<td>19</td>
<td>13</td>
<td>5.2</td>
</tr>
<tr>
<td>C$^{2+}$ + O$^{+}$</td>
<td>29</td>
<td>18</td>
<td>4.9</td>
</tr>
<tr>
<td>C$^{2+}$ + O$^{+}$</td>
<td>50</td>
<td>27</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Difference measurements the situation is different since for every count the forward as well as the backward emitted particle has to reach the detector. So, for a good signal to noise ratio the backward emitted ions need a higher transmission, and more generally the transmission of the forward and backward emitted particles should not differ too much. This is achieved by increasing the extraction voltage together with a larger diaphragm. However, for a good analysis it is important that for the ions with a KER in the region of interest the transmission is less than 10% (section 2.3.3 assumption ii). The measurements have been performed with an extraction field of 150 V/cm and a diaphragm of 6 mm. For these settings the 10% transmission limit for backward emitted O$^+$ is found at a kinetic energy release of 10 eV.

In the time difference spectrum as plotted in figure 5.7a the first peak (around 2 μs) corresponds to the situation where the time measurement has been started by a backward emitted C$^+$ and stopped by a forward O$^+$, while the second peak is due to a start by a forward C$^+$ and a stop by the corresponding backward O$^+$. The distance between these two peaks is twice as large as the time difference between a forward and a backward emitted fragment in a singles spectrum measured with the same settings. For this reason this time difference spectrum lends itself for an analysis as described in section 2.3.3 although it is measured with a relative high extraction voltage.

Besides the C$^{++}$ + O$^+$ peaks there are two peaks corresponding to the C$^{2+}$ + O$^+$ combinations. The position of the O$^{2+}$ + C$^+$ contribution is marked, but the signal is too low to be sepa-
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Time difference (µsec) 1.5 2.0 2.5 3.0 6.0 6.5 7.0
Counts 0 20 40 60 80

Kinetic energy release (eV) 0 1 0 2 0 3 0
Yield 0 20 40 60

C$^2+$ - O$^+$
O$^2+$ - C$^+$

a) C$^-$ - O$^+$
O$^2+$ - C$^+$
C$^+$ - O$^+$
C$^2+$ - O$^+$

Figure 5.7: a) Total time-difference spectrum of ion pairs produced in 4 keV/amu He$^+$ on CO collisions. The kinetic energy distributions are shown in b) and c) for C$^+$ - O$^+$ and C$^2+$ - O$^+$ ion pair formation, respectively. The peaks are corrected for the energy dependent detection efficiency.

rated from the background of accidental coincidences. At first instance this is surprising, because from the singles spectrum we found that the cross section for O$^2+$ + C$^+$ pair production is only 2.4 times smaller than the one for C$^2+$ + O$^+$. However, also the energy distribution has to be taken into account. Due to the higher kinetic energy release by dissociation into O$^2+$ + C$^+$ the efficiency for pair detection is roughly a factor 2 lower than for C$^2+$ + O$^+$, leading to a five times lower O$^2+$ + C$^+$ signal, which is too small to exceed the background.

The kinetic energy distributions are shown in figure 5.7b and 5.7c. The peaks are corrected for the energy dependent detection efficiency. Since the efficiency for pair detection is limited by the detection efficiency of the fragment with the lowest transmission, the correction function of this fragment is used for the peak correction. The different energy contributions are fitted as described in the previous section. The results are listed in table 5.3 together with the statistical errors in the relative yields. The normalised values from table 5.2 are also tabulated.

As mentioned in the previous section, the values in table 5.2 are determined from the TOF spectra using the results from the time-difference spectra. If we compare the coincidence spectra (fig 5.7) with the singles spectra from figure 5.6 we see that the low energy component around 0 eV in the singles spectrum of C$^+$ is not found in the coincidence C$^+$ - O$^+$ distribution. This observation supports the identification of the low energy component as a result of the dissociation of CO$^+$ into a C$^+$ ion and a neutral O.

From the comparison between the kinetic en-
Table 5.3: Kinetic energy distributions for C\(^+\) O\(^+\) and C\(^2+\) O\(^+\) ion pairs determined from the coincidence time-difference spectra compared with the normalised values from the TOF spectra.

<table>
<thead>
<tr>
<th>Products</th>
<th>KER (eV)</th>
<th>FWHM (eV)</th>
<th>Rel. yield</th>
<th>Error</th>
<th>Rel. yield</th>
<th>TOF</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(^+) O(^+)</td>
<td>8</td>
<td>6</td>
<td>28</td>
<td>15</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>C(^+) O(^+)</td>
<td>16</td>
<td>8</td>
<td>61</td>
<td>16</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>C(^+) O(^+)</td>
<td>27</td>
<td>8</td>
<td>11</td>
<td>22</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>C(^2+) O(^+)</td>
<td>20</td>
<td>7</td>
<td>54</td>
<td>20</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>C(^2+) O(^+)</td>
<td>28</td>
<td>10</td>
<td>46</td>
<td>33</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>C(^2+) O(^+)</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td>17</td>
<td></td>
</tr>
</tbody>
</table>

Energy distribution of the coincidence C\(^2+\) O\(^+\) peak and the C\(^2+\) singles we deduce that the 9 eV KER component in the singles spectrum is the result of the dissociation path: CO\(^2+\) → C\(^2+\) O. For the 50 eV contribution which is found in the singles spectra and not in the coincidence ones the situation is different. Because it is found in all four TOF spectra it is probably an artifact from the correction method. As discussed in the previous section the accuracy of the method decreases with increasing kinetic energy (figure 5.5).

So the C\(^+\) TOF spectrum includes contributions of C\(^+\) fragments from dissociation of CO\(^+\), CO\(^2+\) and CO\(^3+\). To compare the shape of the C\(^+\) O\(^+\) yield from the coincidence spectrum with the one deduced from the singles spectra of figure 5.6 we have subtracted the components ascribed to the dissociation of CO\(^+\) and CO\(^3+\) from the C\(^+\) and O\(^+\) singles spectra. The result is shown in figure 5.8. We see that the shapes of the C\(^+\) and O\(^+\) yields deduced from the singles spectra are almost equal. The coincidence peak which is scaled to the singles spectra is somewhat narrower but is also made up from the same components as tabulated in table 5.3. From the comparison we conclude that the contribution of the CO\(^+\) related fragments to the part of the singles spectrum above 3 eV is very small.

5.4 Discussion

In He\(^{2+}\) on CO collisions we have found single, double, and triple ionisation leading to the products as listed in table 5.2. The production of CO\(^4+\) is very unlikely on potential energy grounds and is not observed in the spectra. The ionisation and subsequent dissociation processes are discussed below in the picture of the classical over-
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Figure 5.8: Comparison of the shape of the coincidence \( \text{C}^+ + \text{O}^+ \) ion pair yield with the ones determined from the singles spectra. Full curve, \( \text{C}^+ + \text{O}^+ \) yield from time-difference spectrum; broken curve, \( \text{C}^+ \) yield from singles spectrum reduced with the low energy component associated to \( \text{C}^+ + \text{O} \) and the \( \text{O}^{2+} \) yield except from the 9 eV KER component associated to \( \text{C} + \text{O}^{2+} \); chain curve, \( \text{O}^+ \) yield from singles spectrum reduced with the low energy component associated to \( \text{C} + \text{O}^+ \) and the \( \text{C}^{2+} \) yield except from the 9 eV KER component associated to \( \text{C}^{2+} + \text{O} \).

Barrier model. In addition the results of \( \text{ab initio} \) molecular-orbital calculations of Krishnamurthi et al. (1991) [84] and Lablanquie et al. (1989) [72] are used.

5.4.1 Franck–Condon principle

For simplification of the discussion we assume that the distance between the nuclei of the CO molecule remains fixed during the collision. This assumption is based on the comparison of the molecular rotation and vibration times, \( \sim 10^{-11} \) s and \( \sim 10^{-14} \) s, respectively, with typical collision times of \( 10^{-15} - 10^{-16} \) at 4 keV/amu. Furthermore, it is important that at collision energies in the keV range most of the charge exchange processes take place at relative large distances, some 5 a.u..

From an experimental study of vibronic excitation in \( \text{He}^+ \) on \( \text{N}_2 \) and CO collisions, Dhuiq et al. [85] conclude that the so-called Franck-Condon principle is applicable in the \( \text{He}^+ + \text{N}_2 \) collisions above 0.15 keV/amu collision energy. In the case of CO, deviations from the FC distribution are found up to 0.25 keV/amu, which are ascribed to long-range charge dipole interactions. If we extrapolate their results to higher collision energies we conclude that above 0.5 keV a FC type vibrational distribution should be found. This implies that in the energy range of our experiments (4 keV/amu) we can describe an electronic transition as a vertical transition in the potential energy diagram.

5.4.2 Single ionisation

The electronic configuration of the neutral CO molecule is: \( 1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2 \) for its ground state, which has a \( ^1\Sigma^+ \) symmetry. In a collision with a \( \text{He}^{2+} \) projectile CO\(^+\) can be produced by one-electron capture from the highest occupied orbitals of CO, \( 1\pi \) and \( 5\sigma \). Low excited electronic states can be populated by excitation of one or two electrons to the \( 2\pi \) orbital. There is very little spectroscopy done on such electronic states of CO\(^+\), but calculations have been performed by Krishnamurthi et al. using all electron, \( \text{ab initio} \).
tio, molecular-orbital methods [84]. The results of these calculations are summarised in table 5.4. The energies of the two lowest dissociation limits are given too.

From table 5.4 we see that the single ionisation potential is 13.7 eV, which corresponds to removal of a 5σ electron from CO. The resulting \( 3\Sigma^+ \) state is stable just as the \( 5\Pi \) and \( 4\Sigma^+ \) states. In the \( \text{He}^{2+} + \text{CO} \) collision experiments no less than about 97% of the produced singly charged molecular ions is in one of these stable \( \text{CO}^+ \) states, while only around 3 percent of the \( \text{CO}^+ \) ions is in a dissociating state after the collision (table 5.2). The high production of stable \( \text{CO}^+ \) ions can be qualitatively understood in the framework of the classical overbarrier model (Niehaus 1986 [13]). Figure 5.9a shows the reaction window for one-electron capture from CO into \( \text{He}^{2+} \). From the position of the reaction window it is evident that one-electron capture into the \( \text{He}^+(n = 2) \) at 13.6 eV is a near resonant process and therefore by far the most dominant channel for one-electron capture.

If we compare this with one-electron capture by \( \text{He}^+ \) projectiles we see a totally different picture, figure 5.9b. Here the preferred binding energy of the captured electron at the \( \text{He}^+ \) projectile as calculated with the overbarrier model lies just in between the \( n = 2 \) and the \( n = 1 \) states. So for this system capture of the outermost 5σ electron from CO is unlikely and we can expect a relatively higher population of unstable excited states. Measurements of \( \text{He}^+ \) on CO (not presented here) confirm this expectation. In those experiments we have measured a \( \text{CO}^+ \) production which is smaller than the low energy \( \text{C}^+ \) yield which stems from the dissociation of \( \text{CO}^+ \) into \( \text{C}^++\text{O} \).

Even though in the \( \text{He}^{2+} \) case the fraction of dissociating states populated in the collision is very low, there is a clear \( \text{C}^+ \) peak around 0 eV in the TOF spectrum. This prominent low energy \( \text{C}^+ \) fragment contribution together with a much smaller low energy \( \text{O}^+ \) yield is also observed by Krishnamurthi et al. [84] for one electron capture.

![Figure 5.9](image.png)
in CO$^2+$ on He. From their theoretical results they conclude that it is very likely that the lowest $^4\Delta$ state is the intermediate CO$^+$ state. The total KER by dissociation of this electronic state to C$^+(3P_0)$ + O$(^3P_0)$ is 0.4 eV. However, since the ground state of CO is a singlet, the CO$^+$ formed in a charge exchange process with He$^+$ will be most likely in a doublet state. So, in our experiment the $^4\Delta$ state is unlikely and the $^2\Pi_{1\Sigma}$ state with a KER of 1.58 eV is the most probable candidate.

The fact that there is almost no low energy O$^+$ formation can be explained by the lack of excited states just above the lowest dissociation limit for O$^+$ formation, i.e.: C$(^3P_0)$ + O$(^4S_u)$. The lowest electronic state associated to this dissociation limit is the $^6\Sigma^+_u$ state. But in a collision system the population of this state is spin forbidden. It is possible that dissociation of highly excited states to higher-lying limits results in low energy O$^+$ fragments, but there is no theoretical information on such states.

### 5.4.3 Double ionisation

About 26% of the molecular ions produced in the collision process is double ionised. Double ionisation of CO will preferably occur by capture of two electrons or transfer ionisation from the high occupied $1\pi$ and $5\sigma$ orbitals, possibly with simultaneous excitation to initially unoccupied orbitals. Spin conservation rules allow population of intermediate CO$^{2+}$ states with only singlet or triplet spin multiplicity, so states with higher multiplicity are not considered. The kinetic energy released by dissociation depends on the excited state of the CO$^{2+}$ ion and the dissociation limit. So from the measured KER values we can probably determine which states are populated in the collision. In our C$^+$ + O$^+$ spectra we have observed three

### Table 5.4: Excitation energy in eV from the ground state of CO to various electronic states of CO$^+$ calculated by Krishnamurthi et al. [17]. (A) corresponds to the C$^+(3P_0)$ + O$(^3P_0)$ dissociation limit at 21.69 eV and (B) corresponds to the C$(^3P_g)$ + O$^+$(4$S_u$) limit at 23.37 eV [17].

<table>
<thead>
<tr>
<th>Electronic state</th>
<th>Symmetry</th>
<th>Limit</th>
<th>PE</th>
<th>KER</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4\sigma^21\pi^25\sigma^1$</td>
<td>$^2\Sigma^+_{(t)}$</td>
<td>A</td>
<td>13.66</td>
<td></td>
</tr>
<tr>
<td>$4\sigma^21\pi^25\sigma^2$</td>
<td>$^2\Pi_{(t)}$</td>
<td>A</td>
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<tr>
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<td></td>
</tr>
<tr>
<td>$4\sigma^21\pi^25\sigma^21\pi^1$</td>
<td>$^4\Delta_{(t)}$</td>
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<td>22.11</td>
<td>0.42</td>
</tr>
<tr>
<td>$4\sigma^21\pi^25\sigma^22\pi^1$</td>
<td>$^2\Pi_{(t)}$</td>
<td>A</td>
<td>23.27</td>
<td>1.58</td>
</tr>
<tr>
<td>$4\sigma^21\pi^25\sigma^12\pi^2$</td>
<td>$^4\Pi_{(t)}$</td>
<td>A</td>
<td>26.48</td>
<td>2.74</td>
</tr>
<tr>
<td>$4\sigma^21\pi^25\sigma^22\pi^2$</td>
<td>$^6\Sigma^+_{(t)}$</td>
<td>B</td>
<td>28.63</td>
<td>2.25</td>
</tr>
</tbody>
</table>
components as tabulated in table 5.3. First we focus on the low energy side and try to explain the contribution around 8 eV.

Various electronic configurations, symmetries and dissociation limits of lower-lying states are shown in table 5.5. The values of kinetic energy release predicted from different calculations are presented too [86,72,84]. For some states the results of the various calculations are rather different. However, the few experimental results presented by Lablanquie et al. show the best agreement with their theoretical data [72]. Figure 5.10 shows the potential-energy curves of the lowest electronic states of CO\(^{2+}\) as calculated by Lablanquie et al. [72]. In this figure the position of the 8 eV contribution is depicted with respect to the first dissociation limit. The shaded area reflects the experimentally found full width at half maximum (FWHM).

From figure 5.10 we see that the \(3\Sigma^-\) is a good candidate for the observed 8 eV contribution. Due to the steep slope of this repulsive curve in the Franck-Condon zone it has a FWHM of around 3.0 eV. The \(1\Delta\) state lies just on the edge of the shaded area, but relative to the second dissociation limit the KER is 7.2 with a FWHM of 2.5 eV. So also the \(1\Delta\) state is a good candidate.

From the lower-lying states the \(1\Sigma^+_\ell\), \(1\Pi\ell\) and the \(3\Sigma^+_\ell\) states lead to metastable molecular ions since the predissociation via \(3\Sigma^-\) is either spin or symmetry forbidden. For all these states the potential energy maximum is more than 2.5 eV above the energy at the equilibrium distance \(R_e\) of CO. Because of this also dissociation by a tunnelling mechanism is expected to be very slow.

Figure 5.10: Potential energy curves for the lowest electronic states of CO\(^{2+}\), reproduced from figures 8 and 9 of ref. [72]. The shaded area reflects the position and FWHM of the experimentally found KER-distribution component of 8 eV with respect to the lowest dissociation limit (A). The three lowest dissociation limits are marked by capitals: (A), \(C^+ (^2\Pi_u) + O^+ (^4\Sigma_u^+);\) (B), \(C^+ (^2\Pi_u) + O^+ (^2\Delta_u);\) (C), \(C^+ (^2\Pi_u) + O^+ (^2\Pi_u)\).

The life times of the \(1\Sigma^+_\ell, 1\Pi\ell\) singlet states are \(\geq 9 \mu s\) (Curtis et al. [67]), which explains the small CO\(^{2+}\) contribution in our spectra. (Figure 5.3). The life time of the \(3\Sigma^-\) state is unknown, but expected to be long enough \((\geq 1 \mu s)\) that it does not contribute to the \(C^+ + \text{O}^+\) signal.

Molecular ions which dissociate in the detector hardly contribute to the signal. Only the fragments coming from molecules with the internu-
Dissociation of CO induced by electron transfer to He$^+$ ions

Table 5.5: Excitation energy in eV from the ground state of CO to various electronic states of CO$^{2+}$ calculated by Wetmore et al. [20] (Ref. a), Lablanquie et al. [5] (Ref. b) and Krishnamurthi et al. [17] (Ref. c). The lowest dissociation limits are [5]: (A), $C^+ (2P_u) + O^+ (4S_u)$ at 35.99 eV; (B), $C^+ (2P_u) + O^+ (2D_u)$ at 39.3 eV; (C), $C^+ (2P_u) + O^+ (2P_u)$ at 41 eV; (D), $C^+ (4P_g) + O^+ (4S_u)$ at 41.3 eV.

<table>
<thead>
<tr>
<th>Electronic state</th>
<th>Symmetry</th>
<th>Limit</th>
<th>Ref. a PE</th>
<th>Ref. a KER</th>
<th>Ref. b PE</th>
<th>Ref. b KER</th>
<th>Ref. c PE</th>
<th>Ref. c KER</th>
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</thead>
<tbody>
<tr>
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<td>$^3\Pi_{(1)}$</td>
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<td>5.0</td>
<td>40.6</td>
<td>4.6</td>
<td>41.2</td>
<td>5.2</td>
</tr>
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<td>$^1\Sigma^+_{(1)}$</td>
<td>B</td>
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<td>41.1</td>
<td>1.8</td>
<td>41.0</td>
<td>1.7</td>
</tr>
<tr>
<td>4σ$^2$1π$^3$5σ$^1$</td>
<td>$^1\Pi_{(1)}$</td>
<td>B</td>
<td>41.6</td>
<td>2.3</td>
<td>41.2</td>
<td>1.9</td>
<td>41.6</td>
<td>2.3</td>
</tr>
<tr>
<td>4σ$^2$1π$^4$5σ$^1$</td>
<td>$^3\Sigma^+_g$</td>
<td>B</td>
<td>48.7</td>
<td>9.4</td>
<td>42.5</td>
<td>3.2</td>
<td>43.1</td>
<td>3.8</td>
</tr>
<tr>
<td>4σ$^2$1π$^2$5σ$^2$</td>
<td>$^3\Sigma^-_{(1)}$</td>
<td>A</td>
<td>43.4</td>
<td>7.4</td>
<td>44.4</td>
<td>8.4</td>
<td>45.5</td>
<td>9.5</td>
</tr>
<tr>
<td>4σ$^2$1π$^3$5σ$^2$</td>
<td>$^1\Sigma^+_u$</td>
<td>C</td>
<td>48.4</td>
<td>7.4</td>
<td>45.3</td>
<td>4.3</td>
<td>46.5</td>
<td>5.5</td>
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<tr>
<td>4σ$^2$1π$^2$5σ$^2$</td>
<td>$^1\Delta_{(1)}$</td>
<td>B</td>
<td>47.0</td>
<td>7.7</td>
<td>46.5</td>
<td>7.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4σ$^2$1π$^2$5σ$^1$2π$^1$</td>
<td>$^3\Pi_{(1)}$</td>
<td>B</td>
<td>48.3</td>
<td>9.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4σ$^1$1π$^4$5σ$^1$2π$^1$</td>
<td>$^3\Sigma^+_{(1)}$</td>
<td>C</td>
<td>48.9</td>
<td>7.9</td>
<td>46.7</td>
<td>5.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4σ$^2$1π$^3$5σ$^1$</td>
<td>$^1\Sigma^+_{(11)}$</td>
<td>C</td>
<td>58.6</td>
<td>17.6</td>
<td>49.3</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4σ$^1$1π$^3$5σ$^1$2π$^1$</td>
<td>$^3\Sigma^+_{(1V)}$</td>
<td>D</td>
<td>60.4</td>
<td>19.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
clear axis parallel to the direction of propagation can be detected. However their flight times are shifted towards the ones of the metastable molecular ion and therefore they contribute to the background which is very low in our case.

The lowest state of CO\(^{2+}\) is a \(^3\Pi\(_{1/2}\)\). This state is expected to predissociate rapidly via the \(^3\Sigma\(_{3/2}\)\) state, because the \(^3\Pi \leftrightarrow ^3\Sigma\) transition is allowed by the Kronig selection rules \([87]\). For dissociation to \(C^+(2P_u) + O^+(4S_u)\) the kinetic energy release is around 5.0 eV (table 5.5). However, the KER also depends on the vibrational level populated in the collision. As discussed in section 5.4.1, we assume that the charge transfer process is a vertical Franck-Condon transition so the population of the final state is a projection of the \(^1\Sigma^+\) ground state of CO. The inner and outer classical turning points of the \(v = 0\) level of the ground state are 1.08 and 1.18 Å, respectively. The corresponding vibrational levels of the \(^3\Pi\(_{1/2}\)\) state at these internuclear distances are \(v = 3\) and \(v = 0\), respectively (Wetmore et al.) \([86]\). Dissociation of \(^3\Pi\(_{1/2}\)(v = 3)\) will lead to 0.6 eV extra compared to the values of table 5.5. Independent experimental investigations as reported by Wetmore et al. \([86]\) and Krishnamurthi et al. \([84]\) have determined the energy of a predissociating state at \(5.5 \pm 0.3\) eV above one of the dissociation limits, which is in both papers ascribed to the \(^3\Pi\(_{1/2}\)\) state.

Although in figure 5.10 the potential energy curve for the \(^3\Pi\(_{1/2}\)\) state lies mainly outside the shaded area, the KER of \(5.5 \pm 0.3\) eV corresponds to a potential energy of 41.5 eV which indicates that this state is probably populated in the collision process. To estimate the contribution of the \(^3\Pi\(_{1/2}\)\) state to the 8 eV peak in the coincidence spectrum (fig 5.7), we have fitted this spectrum again with one contribution fixed at 5.5 eV and one fixed at 8.6 eV and leaving the other two contributions unchanged. Doing so we found that a possible contribution of the \(^3\Pi\(_{1/2}\)\) state to the total \(C^+ + O^+\) peak is less than 4%. From this result together with the small fraction of (meta)stable CO\(^{2+}\) which we have observed we conclude that after charge exchange with He\(^{2+}\) the CO\(^{2+}\) ion is mainly in an excited state above 44 eV.

The main contribution to the spectrum of figure 5.7 is found around 16 eV. This indicates that high excited states with potential energies above 55 eV are populated. However at potential energies above 50 eV the density of electronic states of CO\(^{2+}\) becomes so high that population of single well resolved states is no longer possible. To compare our results with the outcome of other experiments we take a look at the average value of the total kinetic energy distribution. For the 4 keV/amu He\(^{2+}\) on CO the average value is 15 eV. This is a little higher than the 13.5 eV which is measured with photoionisation using 110 eV synchrotron radiation \([72]\). In collisions of 97 MeV Ar\(^{14+}\) projectiles on neutral CO molecules, Sampoll et al. (1992) measured an average total kinetic energy of 20±1 eV for the production of \(C^+ + O^+\) ion pairs \([73]\). This indicates that in these experiments higher excited state are populated than in our low energy collision experiments.

The weak population of the lower excited states and the maximum around 16 eV is suggested by the overbarrier model. This is discussed in chapter 6 in relation to collision energy and projectile charge dependent collisions.
In comparison with other experiments, a strikingly good agreement is found with the photoionisation experiments of Hitchcock et al. [71]. They have measured the kinetic energy distribution by pair production following C(1s) ionisation at 305 eV. By deconvolution of the distribution, they have obtained five contributions at 4.0, 8.6, 12.5, 17.0 and 28 eV with relative intensities of 2, 31, 15, 40 and 12, respectively. If we neglect the 2% at 4.0 eV and add the 12.5 to the 17.0 eV contribution we obtain three components i.e.: 8.6, 15.8 and 28 eV with weights 31, 55 and 12, respectively, which reflects almost the same energy distribution as in our measurements of 4 keV/amu He\(^{2+}\) on CO.

### 5.4.4 Triple ionisation

About 18% of the molecular ions produced in the collision with 4keV/amu He\(^{2+}\) is triply ionised while 26% is doubly ionised (table 5.2). This fraction is much higher than reported from photoionisation measurements. With 305 eV photons Hitchcock et al. [71] have observed a C\(^{2+}\)+O\(^{+}\) production which is 13 times stronger than the formation of C\(^{2+}\)+O\(^{+}\) pairs, while in our experiments this ratio is 2.1. Sampoll et al. [73] didn’t report cross sections from their measurements, but in a follow-up article by Wohrer et al. [88] the relative yields have been presented. They found a ratio of 2.2.

In our collision experiments the most probable way for triple ionisation is capture of two inner electrons followed by an autoionisation process. There are no indications for the existence of metastable CO\(^{3+}\) states. From our singles TOF spectra we conclude that dissociation dominantly occurs into C\(^{2+}\)+O\(^{+}\). The intensity of the C\(^{2+}\)+O\(^{2+}\) dissociation path is a factor 2.5 less. This is almost the same factor as is found by Wohrer et al. [88]. In the photoionisation experiments of Hitchcock et al. [71] the C\(^{2+}\)+O\(^{2+}\) yield could not be determined since the signal was very weak and not well resolved.

The 20 and 28 eV kinetic energy components show up in the same ratio (table 5.3) in the time difference spectrum and in the TOF spectrum. They will be discussed below. There are only a few calculated potential energies for possible excited states of CO\(^{3+}\) presented by Mathur et al. [75]. For the lowest-energy electronic states, \(^3\Pi\) and \(^4\Sigma^-\) they found a value of about 83 eV compared to the CO \(^1\Sigma^+\) ground state. Lablanquie et al. have observed the photoionisation threshold for C\(^{2+}\)+O\(^{+}\) production at 81\(\pm\)2 eV [72]. If we assume that the \(^4\Sigma^-\) state is the lowest repulsive state of CO\(^{3+}\) which dissociates to the lowest limit, C\(^{2+}\)(\(^1\Sigma_g\)) + O\(^{+}\)(\(^4\Sigma_u\)), with a potential energy of 60.4 eV, the kinetic energy release is the energy difference between the ionisation potential and the dissociation limit i.e.: \(~20\) eV. This is equal to the value of the lowest KER component observed in the experiments. The measured kinetic energy release of 28 eV is caused by the population of higher excited states. This implies that also in CO\(^{3+}\) there are excited states above the repulsive Coulomb curve i.e.: \(q_1g_2/R_0\), which will lead to a KER of \(25\) eV. This result does not agree with observed and calculated KER values for heavy ion impact of Mathur et al. [75]. They assume the excited states to dissociate to higher dissociation limits leading to lower values of kinetic energy.
energy release than expected from a Coulombic model.

Comparison of the energy distribution obtained in our measurements with the one of Hitchcock et al. obtained by inner shell photoionisation indicates that, just as for double ionisation, the same excited states are populated in the same ratio. For 305 eV photons they report two components of (20 eV, 10 eV, 1.0) and (30 eV, 20 eV, 1.0) average energy, width and weights, respectively [71]. Sampoll et al. [73] observed an average total kinetic energy of 37 eV for this case which is significantly higher than the 24 eV produced in our experiments.

5.5 Conclusion

We have studied the dissociation of multicharged CO\textsuperscript{q+} ions (q \leq 3) produced in collisions with 4 keV/amu He\textsuperscript{3+}. Time-of-flight and coincidence time-difference measurements are performed. To transform the TOF spectra into kinetic energy distributions a correction method is used as described in chapter 2. From the KER distribution we have determined different contributions associated with different dissociation channels.

We have found that during the charge exchange process molecular ions are formed up to triply charged, while only CO\textsuperscript{+} and CO\textsuperscript{3+} molecular ions have been seen to survive long enough to be detected as molecular ions. Almost all the CO\textsuperscript{+} is produced in one of the stable states. This can be understood in the picture of the overbarrier model. Since one-electron capture of the weakest bound electron into He\textsuperscript{3+} is a near resonant process it is the dominant channel contributing to the formation of CO\textsuperscript{+}. Double ionisation of CO leads preferably to excited CO\textsuperscript{2+} states which mainly dissociate into C\textsuperscript{+} + O\textsuperscript{+}. Although the lowest potential energy curves of CO\textsuperscript{2+} are known with sufficient accuracy it is not possible to determine unambiguously which states are populated. However, from the low yield around 5.5 eV we conclude that the population of the lowest state of CO\textsuperscript{2+} is less than 4%.

The KER distributions obtained for CO\textsuperscript{2+} and CO\textsuperscript{3+} dissociation have average values of 15 eV and 24 eV, respectively, i.e. almost the same as measured for photoionisation by Hitchcock et al. [71]. Comparison of our results with Ar ion impact ionisation results of Sampoll et al. [73] indicates that keV He\textsuperscript{2+} collisions lead to population of lower excited states than collisions with MeV Ar\textsuperscript{14+}.

The transient CO\textsuperscript{3+} state has been found to dissociate into C\textsuperscript{2+} + O\textsuperscript{+} and C\textsuperscript{+} + O\textsuperscript{2+} in the ratio of 2.5 to 1. This is nearly the same ratio as is found for heavy ion impact by Wohrer et al. [88] in spite of the fact that different excited states are populated. The observed ratio between the production of CO\textsuperscript{3+} and CO\textsuperscript{2+} transient ions is almost equal to the one for fast heavy ion impact but much higher than that reported for photoionisation.