Molecular dissociation induced by electron transfer to multicharged ions
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Chapter 6

Kinetic energy release in molecular dissociation: projectile charge and collision energy dependence

Dissociation products of CO have been measured in coincidence with each other for collisions with He\(^{2+}\) and O\(^{7+}\) in the energy range of 2 to 11 keV/amu. Fragments from the dissociation of CO\(^{q+}\) transient ions have been observed for 2 \(\leq q \leq 4\). From the time-difference spectra we have determined the kinetic energy of the charged fragments. We have found that in spite of the fact that O\(^{7+}\) carries much more potential energy than He\(^{2+}\), in collision with CO it induces less kinetic energy release at C\(^+\)+ O\(^+\) formation. Furthermore we have observed that with increasing impact energy the kinetic energy of the fragments decreases. These observations are qualitatively understood in the picture of the overbarrier model. By considering three-electron processes we were able to calculate the potential energies of the populated excited states in CO\(^{2+}\) from the binding energies of the recaptured electrons. From the kinetic energy release threshold for C\(^{2+}\)+ O\(^{2+}\) ion pair formation we have determined the lowest potential energy of the transient CO\(^{4+}\) molecular ion to be 134.5 ± 2 eV with respect to the CO ground state.
6.1 Introduction

Ionisation of molecules can lead to the formation of unstable molecular ions which will eventually decay into various fragments. Time-of-flight spectra of molecular ions and charged fragments (dissociation patterns) tells us something about the stability of the molecules and the various dissociation channels. In the past, ionisation and molecular dissociation due to photon or electron impact have been extensively studied [12, 72, 71]. Furthermore, various dissociation patterns have been studied using fast highly charged heavy ions [73-75]. These patterns are significantly different from the ones induced by photoionisation since the collision of a highly charged ion on a molecule will, with a high probability, result in a simultaneous removal of several electrons, whereas during photon or electron impact preferably only one electron is removed. Besides, in collisions between MeV highly charged ions and molecules the total kinetic energy of the fragments is higher [73].

Slow multicharged ion collisions with molecular targets are assumed to be more "gentle" than collisions with fast heavy ions due to the relatively large impact parameters at which electrons can be captured nearly resonantly [76]. The ionisation and dissociation is assumed to take place in the following two steps:

\[ A^{q^+} + \text{CO} \longrightarrow A_{(q-r+s)}^{(q-r+s)+} + \text{CO}_{r-s}^{(r-s)+} + e^- \quad (6.1) \]

and

\[ \text{CO}^{r+} \longrightarrow \text{C}^{t+} + \text{O}^{(r-t)+} + U_{KER} \quad (6.2) \]

where \( U_{KER} \) is the kinetic energy released in the dissociation.

As discussed in chapter 5, collisions between 4 keV/amu He\(^{2+}\) on CO lead to an average kinetic energy released in the dissociation of these molecular ions which is indeed lower than reported for fast highly charged ion impact. However from the comparison of our measurements with calculations of electronic states of CO\(^{q^+}\), with \( q \leq 3 \), we have seen that in keV He\(^{2+}\) collisions on CO the low-lying electronic states of CO\(^{2+}\) are nearly not populated.

In this chapter we will show that the population of excited CO\(^{q^+}\) states can be explained qualitatively in the picture of the classical over-barrier model. It will be shown that in collisions of He\(^{2+}\) on CO capture of the outer two electrons is unlikely on grounds of availability of states, while capture of the second and third electron is a resonant process. The latter process leads to the population of highly excited states. To check this explanation we have measured the dissociation patterns from CO colliding with He\(^{2+}\) ions at different impact energies. Furthermore we have measured the kinetic energy released in the dissociation of CO induced by O\(^{7+}\) ions.

For collisions between O\(^{7+}\) and CO the charge exchange picture is different. Here capture of the outer two electrons is resonant with a large number of O\(^{5+}\) states. To check whether this leads to the population of lower excited states of CO\(^{q^+}\) we will compare the kinetic energy distributions resulting from O\(^{7+}\) collisions with the ones from He\(^{2+}\). It will be shown that contrary to the fact that O\(^{7+}\) carries much more potential energy, in collision with CO it induces less kinetic energy at
C\(^+\) + O\(^+\) formation than He\(^{2+}\).

6.2 Experiment

A continuous beam of \(^{3}\)He\(^{2+}\) or O\(^{9+}\) ions is extracted from the ECR source at 3 to 16 kV. The ion beam is impinging on a gaseous CO molecular target with a full width at half maximum of 3 mm. The target pressure was about 0.4 mPa and the beam intensity was adjusted to \(\sim 100\) pA. The resulting molecular ions and charged molecular fragments are extracted perpendicularly to the ion beam into a reflectron mass spectrometer thereby passing a diaphragm with a diameter of 6 mm. The set-up including the reflectron is described in detail in section 2.3.

With a time-to-amplitude converter (TAC) we have measured time-difference spectra by starting the TAC on the first arriving fragment and using the signal from the second charged fragment as a stop. With this coincidence technique only C\(^{9+}\) + O\(^{+}\) ion pairs are detected. To avoid that the TAC starts and stops at the same input signal the start signal is delayed by some 50 ns.

As discussed in section 2.3.3 we can exploit the fact that at low extraction field most of the energetic fragments will be intercepted by the entrance diaphragm of the spectrometer. Only particles ejected within a small angle with respect to the detection axis can be detected. This gives rise to a double peak structure in the singles TOF spectra as shown in figure 5.4. Ions with their initial velocity towards the spectrometer (forward emitted fragments) have a shorter flight time than the ones with the initial velocity in the opposite direction (backward emitted fragments) since the latter ones first have to be turned around in the electric field before they can reach the spectrometer aperture.

In the coincidence measurements, for every measured C\(^{9+}\) + O\(^{+}\) ion pair one of the fragments is emitted in forward direction and one in backward direction. Therefore, there are two combinations leading to two peaks in the time spectrum which are separated by a time interval (\(\Delta T\)) which is equal to the sum of the time differences between the forward and backward emitted C\(^{9+}\) fragments and between the forward and backward emitted O\(^{+}\) fragments. Analogous to equation (2.5) the relation between \(\Delta T\) and the kinetic energy release (\(U_{KER}\)) is given by

\[
\Delta T = \frac{q + r}{q r E} \sqrt{\frac{8 \mu U_{KER}}{m_1 m_2}}
\]

where \(q\) and \(r\) are the charge states of the fragments, \(E\) is the extraction field and \(\mu = m_1 m_2 / (m_1 + m_2)\) with \(m_1, m_2\) the masses of the fragments.

We have used this equation to transform the time-difference spectra in to kinetic energy distributions. Doing so, we assume that an ion pair with a well defined initial kinetic energy contributes to a narrow time interval in the time-difference spectrum. This assumption holds if the fragments are only detected when they are emitted within a small angle with respect to the detection axis. As discussed in section 2.3.3 this condition is sufficiently met if less than 10\% of the fragments can pass the entrance diaphragm of the spectrometer.

The transmission of the fragments depends on
the initial kinetic energy. We have therefore corrected our coincidence data by multiplication with $1/k$, where $k$ is the detection efficiency of the fragment with the lowest transmission. The energy dependences of the $1/k$ correction functions are shown in figure 6.1 for an extraction field of 90 V/cm which is used in the O$^{7+}$ measurements. From this figure we see that for a total kinetic energy above 8 eV the correction factor for the singly charged particles is $>10$, thus justifying the assumption of well defined relation between $\Delta T$ and kinetic energy release. The He$^{2+}$ on CO collision experiments are performed with an extraction field of 150 V/cm. For this case the $\leq10\%$ transmission limit for backward emitted O$^+$ is found at a kinetic energy release of $\geq10$ eV.

### 6.3 Experimental results

We have measured coincidence time-difference spectra for 2 keV/amu, 4 keV/amu and 10.7 keV/amu He$^{2+}$ on CO collisions. In figure 6.2 the uncorrected time-difference spectrum for collisions with 2 keV/amu He$^{2+}$ ions is shown. In the spectrum the first peak (around 2 μs) corresponds to the situation where the time measurements have been started by a backward emitted C$^+$ and stopped by a forward O$^+$, while the second peak is due to a start from a forward C$^+$ and a stop from the corresponding backward O$^+$. Two peaks associated with the C$^{2+}$ + O$^+$ combinations are found at 6 μs and 6.5 μs. The position of the O$^{2+}$ + C$^+$ contribution is marked, but the signal is too low to be separated from the background.

Furthermore we see an intensity difference between two peaks corresponding to the same ion pair. This is due to the difference in detection efficiency. For example, the energy dependence of the detection efficiency for the first C$^+$ + O$^+$ is equal to the one for backward emitted C$^+$ ions, while that for the second peak equals the one for backward emitted O$^+$ ions. As we can see in figure 6.1, the transmission for backward emitted
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Figure 6.2: Time-difference spectrum of ion pairs produced in 2 keV/amu He\(^{2+}\) on CO collisions.

C\(^+\) is lower than for backward O\(^+\), therefore in the spectrum the first peak is lower than the second one. After correction the peak intensities are more or less the same.

In figure 6.3 the kinetic energy distributions for C\(^+\) + O\(^+\) and C\(^{2+}\) + O\(^+\) ion pair formation are shown for the different collision energies. In the C\(^+\) + O\(^+\) spectra we can roughly distinguish three components at around 8.5 eV, 16 eV and 25 eV by a fit procedure. The fitting process is a free fit except for some restrictions i.e: the functions are Gaussians, the number of Gaussians is chosen in such a way that when an extra Gauss is added this will largely coincide with another contribution, and the second and third components in the C\(^+\) + O\(^+\) spectra have equal width. The sum of the fitted contributions is depicted by a full curve.

From figure 6.3 we see that the ratio between the C\(^+\) + O\(^+\) components changes drastically with

Figure 6.3: Kinetic energy distributions for C\(^+\) + O\(^+\) (first column) and C\(^{2+}\) + O\(^+\) (second column) ion pair formation for different impact energies. The fitted contributions are indicated by the broken curves.
increasing collision energy. In all the $C^{2+} + O^+$ spectra we see a component around 20 eV and one at 30 eV down to 25 eV of which the relative intensity decreases with increasing collision energy. The most striking observation is that for $C^{2+} + O^+$ and probably also for $C^{2+} + O^+$ ion pair formation the average kinetic energy released in the dissociation decreases with increasing collision energy. This is also shown in figure 6.4 in which the average energy release versus the collision energies is plotted.

Figure 6.4: Average kinetic energy release versus collision energy for $C^{2+} + O^+$ (circles) and $C^{2+} + O^+$ (squares) ion pair formation induced by He$^{2+}$ impact (full symbols) and O$^{7+}$ impact (open symbols).

The errors indicated include the statistical errors, the experimental uncertainty in the correction functions due to an uncertainty in the position of the collision centre with respect to the diaphragm, and the uncertainty in the transformation from $\Delta T$ to $U_{KER}$. Due to the low total yields in the time-difference spectra the statistical errors are rather large. For example, in the $C^+ + O^+$ KER spectra for 4 keV/amu He$^{2+}$ collisions the statistical uncertainty increases from around 13% at 10 eV to 20% at 25 eV. The error in the transformation from $\Delta T$ to $U_{KER}$ is mainly caused by the fact that particles with the same initial kinetic energy can be emitted under different angles. Therefore this uncertainty is directly related to the solid angle of the spectrometer and thus to the kinetic energy of the fragments. This is discussed in section 2.3.3. The uncertainty in the determined kinetic energy release due to the time spread of the fragments is around 10% at 10 eV and 4% at 25 eV.

Figure 6.5: Time-difference spectrum of ion pairs produced in 3.5 keV/amu O$^{7+}$ on CO collisions.

A time-difference spectrum for the dissociation of CO induced by 3.5 keV/amu O$^{7+}$ collisions is shown in figure 6.5. In addition to the ion pairs
observed in the He$^{2^+}$ collisions there is a clear contribution from C$^{2^+}+$ O$^+$ ion pair production. Furthermore, compared to the He$^{3^+}$ case, the ratio between C$^{+}$ O$^+$ and C$^{2^+}$ O$^+$ yields is higher for collisions with O$^7^+$. The kinetic energy distributions determined from figure 6.5 are depicted in figure 6.6. The average KER values are plotted in figure 6.4 (open symbols). The average kinetic energy released in C$^{+}$ O$^+$ formation turns out to be much lower than for collisions of He$^{2^+}$ on CO, while the energy distribution for C$^{2^+}$ O$^+$ formation is comparable with the He$^{2^+}$ case. Such a projectile-charge state dependence of the kinetic energy release has been observed before for O$^9^+$/H$^+$ collisions [76,89]. A big difference between He$^{2^+}$ and O$^7^+$ is found in the fact that in the O$^7^+$/CO spectrum (figure 6.6a) an important component shows up around 6 eV which is not present in the kinetic energy distribution induced by He$^{2^+}$. The other fit contributions are centred around 8,5, 13,5 and 17 eV. The distribution for C$^{2^+}$ O$^+$ formation can roughly be distinguished into two components at 39 and 48 eV.

### 6.4 Discussion

#### 6.4.1 Electron transfer

In the previous chapter we have extensively discussed the dissociation of CO induced by 4 keV/amu He$^{2^+}$ collisions. We have focused on determination of the various dissociation channels, comparison with other experimental results and explanation of our results using potential energy curves of several electronic states of CO$^+$.

Figure 6.6: Kinetic energy distributions for C$^{+}$ O$^+$, C$^{2^+}$ O$^+$ and C$^{2^+}$ O$^2^+$ ion pair formation for 3.5 keV/amu O$^7^+$ on CO collisions. The spectra are corrected for the energy dependent detection efficiency. The fitted contributions are indicated by the broken curves. The full curves show the sum of the various contributions.
with \( q \leq 3 \), which have been calculated by various groups.

In this section we will mainly discuss the charge exchange processes in the picture of the overbarrier model [13]. In chapter 1 it is shown that in spite of the molecular nature of CO the overbarrier model, which has been developed for ion-atom collisions, can be used for a description of electron transfer to highly charged ions, because the collision time is short compared to the vibration time of the nuclei in the molecule, and because capture of the outer electrons takes place at large internuclear distances compared to the size of the molecule.

The overbarrier model considers the binding energies of the electrons in the joint Coulomb field of the colliding particles. With the model we can calculate the internuclear distance at which capture takes place and the binding energy of an electron after capture by the projectile or recapture by the target. There is an uncertainty in the binding energy due to the fact that a certain potential barrier height is realised only for a limited amount of time. The uncertainty is reflected in the width of a Gaussian distribution of binding energies around the most probable value (reaction window). The width increases proportional to \( E^{0.25} \), where \( E \) is the collision energy. [57].

### 6.4.2 Collision energy dependence

For calculations with the overbarrier model we have used ionisation potentials of the outer three CO electrons of 13.7, 27.3 and 40 eV, respectively. These values are deduced from the thresholds for CO\(^{3+}\) and CO\(^{2+}\) transient ion production as have been observed by Lablanquie et al. [72] by means of photoionisation, together with the ionisation potential for single ionisation which has been extracted from potential energy curve calculations [84] under the assumption that the internuclear distance between the C and the O remains fixed during the collision.

With the overbarrier model we have calculated the binding energies of the captured electrons in the helium projectile and the recaptured electron in the target. During the collision, on the way in, the third electron can cross the potential barrier at a distance of 0.28 nm which is more than two times the equilibrium internuclear distance \( (R_e) \) of the CO ground state of 0.11 nm. If on the way out two electrons are captured by the helium ion while one is recaptured by the target this will lead to a CO\(^{2+}\) molecular ion which sooner or later will dissociate. The population of excited states is related to the binding energy of the recaptured electron. The kinetic energy of the fragments depends firstly on the excited states of the transient CO\(^{2+}\) ion which are populated in the charge exchange process, and secondly on the final dissociation limit.

The results of the calculations for the total binding energy of the two captured electrons in helium are shown in figure 6.7 for the three possibilities assuming that three electrons are involved in the charge exchange process. The width of the reaction windows are calculated as proposed by Hoekstra et al. [57] for a collision energy of 2 keV/amu. The binding energies of the He\((nl,n'l')\) levels are indicated.

In figure 6.7a the reaction window is drawn for
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capture of the two outer electrons. This is indicated by the string (110) where (1) denotes capture by the projectile and (0) recapture by the target. The position in the string, from left to right, corresponds to the sequence in which the electrons become molecular on the way in of the collision. The summed binding energy of the two outer electrons in CO is 41 eV. According to the overbarrier model the binding energy after capture will be the same in both cases the electrons are bound in the Coulomb field of a doubly charged nucleus. To compare the so found binding energy with the energies of the real $\text{He}(n_l, n_l')$ states, these states are also indicated in the figure. From figure 6.7a it is seen that the reaction window lies in between the $\text{He}(1s, 2l)$ and the $\text{He}(2l, 2l')$ states. This position indicates that capture of the outer two electrons is unlikely.

In figure 6.7b the situation is drawn for capture of the first and third electron (101). The reaction window slightly overlaps with the $\text{He}(1s, 2l)$ states which suggest a somewhat higher probability of this capture channel. This will lead to the population of excited states of $\text{CO}^{2+}$ because it implies recapture of the second electron by the target. The importance of target-ion excitation is discussed in a paper by de Nijs et al. (1993) [90] for $\text{N}^{7+}$ on Ar collisions. As calculated with the overbarrier model the binding energy of this re-captured electron ($E_T$) in $\text{CO}^{2+}$ is 31.6 eV with a FWHM of 11.6 eV. This binding energy corresponds to excited states of the molecular ion with a potential energy of about 49 eV with respect to the CO ground state. This is seen in figure 6.8 where the ground state of CO and the lowest states of $\text{CO}^{2+}$ with $1 \leq q \leq 3$ are sketched to-

Figure 6.7: Reaction windows for two-electron capture in collisions of 2 keV/amu $\text{He}^{3+}$ on CO, as calculated from the classical overbarrier model under the assumption that three electrons are involved in the charge exchange process. Each process is indicated by a string, where (1) denotes capture by the projectile and (0) recapture by the target. The position in the string, from left to right, corresponds to the sequence in which the electrons become molecular on the way in of the collision.
together with the dissociation limits associated with these electronic molecular ion states.

To compare this result with our experimental data we have to deduce a value for the kinetic energy release. Therefore we refer to the results of \textit{ab initio} molecular-orbital calculations of Lablanquie et al. [72] as we did in the previous chapter. However, it should be noted that due to the high density of excited states above 50 eV it is not possible to distinguish between the various states. Furthermore, as stated by Lablanquie et al., the precision of the potential energy calculations decreases with increasing potential energy. As seen from figure 5.10 and table 5.5 it is unlikely that excited states with a potential energy of around 49 eV at \(R_e\) (pre-)dissociate to the lowest dissociation limit. Dissociation to the second or third limit at 39.3 eV and 41 eV, respectively, is more probable. According to the calculation of Lablanquie et al. [72], listed in table 5.5, this will lead to a kinetic energy release of about 8.5 eV.

Figure 6.7c shows the overbarrier model reaction window for recapture of the first electron, string (011). According to the model the binding energy of the excited electron in \(\text{CO}^{2+}\) (ET\(_1\)) is 20.7 eV with a FWHM of 8.1 eV which corresponds to a potential energy of the excited transient ion of about 60 eV (figure 6.8). Here the reaction window overlaps exactly with the He(1s, 2p) states which hints at a strong population of these excited states. The kinetic energy released by (pre)-dissociation to the third, fourth or fifth dissociation limit will be between 16 and 19 eV.

The so found KER values agree with the experimentally found values of 8 and 17 eV for \(\text{C}^+\) + \(\text{O}^+\) formation as indicated by the broken curves

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig6.8.png}
\caption{Schematic drawing of the ground state of \text{CO} and the lowest \text{CO}^{4+} states together with the dissociation limits associated with these electronic molecular ion states. The potential energy of the populated excited states of \text{CO}^{2+} is determined from the binding energy of the recaptured electron, as is indicated by the arrows. ET\(_1\) and ET\(_2\) correspond to the reaction strings (011) and (101), respectively. ET\(_2^*\) indicates the binding energy of a recaptured electron in a (101) process after autoexcitation (see text).}
\end{figure}
in figure 6.3. At 2 keV/amu the yield of the 17 eV component is indeed the highest as predicted by the overbarrier model. However, with increasing collision energy the yield of the 17 eV component decreases relative to the 8 eV one. This can also qualitatively be understood with the overbarrier model. Since the width of the reaction window increases proportional to $E^{0.25}$ [57] the overlap of the (101) window with the He(1s, 2l) states will increase with impact energy. From this it might be expected that the probability of the (101) capture channel will increase with respect to the (011) channel.

In the low energy spectra in figure 6.3 there is a third component at around 25 eV which suggests the population of higher excited transient CO$^{2+}$ ion states than can be explained with the capture channels discussed above. From the figure we see that the occurrence of this component strongly depends on the collision energy. The highly excited states are probably populated in a so called autoexcitation process, as discussed in section 4.7. In such a process the electrons exchange binding energy during the transient molecular phase in the collision when a (HeCO)$^{2+}$ ion is formed by the projectile and the molecular target. Therefore these processes can only occur if the collision time is long enough which explains the dependence on the impact energy [57]. In an autoexcitation process the total binding energy in the molecular phase is assumed to be fixed. For the present system this implies that whenever the third electron is captured by the projectile it makes a transition from the energy level where it is captured (EP3) at 35.5 eV to the real He$^+$ (1s) ground state at 54.4 eV, the gain in binding energy of about 19 eV has to be accounted for by the second electron which is recaptured by the target. So its binding energy reduces from 31.6 eV to only 12.6 eV leading to excited states at around 68 eV, indicated as ET$^+$ in figure 6.8. The dissociation of these states can result in the formation of high energetic fragments as observed in the spectra at low impact energy.

The average kinetic energy released in $C_2^++$ O$^+$ ion pair formation depends on the collision energy as can be seen in figure 6.4. All the KER distribution spectra for $C_2^++$ O$^+$ production of figure 6.3 show an energy component around 20 eV and a second one at higher energy which decreases in energy and relative intensity with increasing impact energy. The energy behaviour of this second component suggests the existence of charge exchange channels comparable with the ones discussed for two-electron removal. However these channels are not found with the overbarrier model, since there is not enough potential energy available in the He$^+$ ion.

On basis of the model we only expect a KER component around 20 eV for capture of the third and fourth electron of CO. These electrons end up in the helium at a binding energy of about 76 eV which is near resonant with the He(1s$^2$) at 79 eV. The outer two electrons are recaptured by the target after which one can be ejected in an autoionisation process, leading to a CO$^{3+}$ transient ion at a potential energy just above the threshold with a maximum of $\sim$84 eV. As discussed in section 5.4 by dissociation of the lower-lying repulsive states of CO$^{3+}$ the fragments will yield a kinetic energy of some 20 eV.
6.4.3 Charge state dependence

Electron transfer to \( O^{7+} \) is substantially different from capture by \( He^{2+} \) because for \( O^{7+} \) capture can take place at larger internuclear distances. Furthermore a large number of states can be populated almost resonantly as can be seen in figure 6.8. In this figure the reaction windows for three possible two-electron capture channels are shown together with the binding energies of the various \( O^{5+}(1s, nl, n'l') \) configurations which are calculated with the Cowan code [91,92].

![Figure 6.9: Reaction windows for two-electron capture in two and three-electron processes in collisions of 3.5 keV/amu \( O^{7+} \) on CO, as calculated from the classical overbarrier model. The binding energies of the \( O^{5+}(1s, nl, n'l') \) levels are indicated.](#)

From figure 6.9 we see that the reaction window for the two-electron process indicated by the string (11) coincides with \( O^{5+}(1s, 4l, n'l') \) states. This supports the experimental observations of figure 6.6a where we see a relatively high yield of low kinetic energy \( C^+ + O^+ \) fragments. The low energy components at 6 eV and 8.5 eV can be explained by the (11) capture channel since by capture of one of the two outer electrons only lower-lying states of \( CO^{2+} \) are populated. As discussed in section 5.4.3 the lowest state, \( ^3\Pi(t) \), is expected to predissociate via the \( ^3\Sigma(t) \) state to \( C^+(2P_u) + O^+(4S_u) \) which yields a kinetic energy of around 5.0 eV (see figure 5.10 and table 5.5). Direct population of the \( ^3\Sigma(t) \) state has almost the same probability since the potential energy of this state is only 3 eV higher. Dissociation via \( ^3\Sigma(t) \) results in a kinetic energy release of \( \sim 8.5 \) eV. So, it is very likely that the \( ^3\Pi(t) \) and \( ^3\Sigma(t) \) states of \( CO^{2+} \) are populated by two-electron capture to \( O^{7+} \).

In the previous part concerned with electron transfer to \( He^{2+} \) we have seen that three-electron processes can contribute to the population of excited states yielding kinetic energies of 8 eV and higher. These processes also occur in \( O^{7+} \) (see figure 6.9) but have a smaller cross section than two electron processes due to the smaller impact parameter which is needed for three-electron processes. The binding energies for the recaptured electrons in the three-electron processes with oxygen are almost equal to the values calculated for charge exchange with helium. So the production of fragments with total kinetic energy above 8 eV as observed in the experiments are probably the result of the population of excited states via a \( (011) \) capture process.

Capture processes involving three or more electrons will lead to the formation of \( C^2+ + O^+ \) and \( C^2++ O^{2+} \) ion pairs. The cross sections for the formation of these ion pairs are smaller than for
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C\(^+\) + O\(^+\) ion pair production as can be seen from the relative yield in figure 6.6.

The kinetic energy distribution of the C\(^2+\) + O\(^+\) ion pairs is comparable to the ones in the helium collision experiments although the statistics is poorer. The main component is found around 20 eV. As discussed before this value corresponds to the population of the lowest energy states of the CO\(^3+\) transient ion. Therefore, we can determine the potential energy threshold for C\(^2+\) + O\(^+\) ion pair formation (figure 6.8). Our measurements support the observation of Lablanquie et al. [72] who have determined the appearance energy by photoionisation to be 81 ± 2 eV. For the production of C\(^2+\) + O\(^2+\) ion pairs the threshold is observed at a kinetic energy release of ~39 ± 2 eV. With respect to the lowest dissociation limit, C\(^2+\)(\(^1\)S) + O\(^2+\)(\(^3\)P), at 95.5 eV this corresponds to a potential energy of the transient CO\(^4+\) molecular ion of around 134.5 ± 2 eV.

The kinetic energy released in a dissociation caused by pure Coulomb repulsion can be calculated as: \(q_1q_2/R_e\), with \(R_e=0.1128\) nm. The so found KER values for C\(^+\) + O\(^+\), C\(^2+\) + O\(^+\), and C\(^2+\) + O\(^2+\) ion pair formation are 12.8 eV, 25.7 eV, and 51.4 eV, respectively. The observed kinetic energy distributions clearly exceed these values except for C\(^2+\) + O\(^+\) ion pair formation where we have measured the highest energy component at 48 eV. This observation supports the intuitive picture that with less electrons involved the dissociation behaves more like Coulomb explosion.

6.5 Conclusions

We have studied the dissociation of CO induced by electron transfer to He\(^2+\) and O\(^7+\) ions. From coincidence time-difference measurements we have determined the kinetic energy of the fragments formed in the dissociation process. We have observed that the kinetic energy distributions strongly depend on the collision energy and the projectile charge state. The average kinetic energy decreases with increasing impact energy or charge state.

Our observations are qualitatively understood in the picture of the overbarrier model. The potential energy of the populated excited states in CO\(^2+\) have been calculated from the binding energies of the recaptured electrons. In this way we were able to explain the observed KER values for C\(^+\) + O\(^+\) formation by He\(^2+\) impact. Furthermore the occurrence of a KER component at around 25 eV could be explained under the assumption that electrons exchange energy during the transient molecular phase in the collision. These so-called auto-excitation processes are assumed to occur only if the collision time is long enough. This explains the dependence on the impact energy.

In charge exchange processes between O\(^7+\) and CO two electron capture is a resonant process which causes the relatively high population of lower-lying excited states in CO. The experimentally found KER values of 6 eV and 8.5 eV for C\(^+\) + O\(^+\) formation are ascribed to the predissociation of the \(^3\)Π\(_{(1)}\) and the dissociation of the \(^3\)Σ\(^−\)\(_{(1)}\), respectively. From the kinetic energy release of C\(^2+\) + O\(^2+\) ion pair formation we have determined
the lowest potential energy of the transient CO$^{4+}$ molecular ion to be 134.5±2 eV with respect to the CO ground state.