Escape of CO$_2^+$ and Other Heavy Minor Ions From the Ionosphere of Mars

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Abstract Ionspheric escape from Mars is an important process for the erosion of the Martian atmosphere. The heavy ion outflow is dominated by O$_2^+$ and O$^+$, however, the Martian ionosphere consists of many more ion species. In the dayside ionosphere below roughly 220 km altitude, CO$_2^+$ is the second most dominant ion, and higher up and in the nightside ionosphere other ions species with a mass near but below that of O$_2^+$ (28–30 Atomic Mass Unit [AMU], e.g., CO$^+$, N$_2^+$, HCO$^+$, NO$^+$, etc.) gain in importance. However, their contribution to the ionospheric outflow is often obscured by the dominant ions O$_2^+$ and O$^+$. Therefore, we perform a peak fitting to the mass spectrum of SupraThermal and Thermal ion outflow. We find that CO$_2^+$ can be seen throughout the Martian magnetosphere, but it escapes only in small amounts at a mean rate of less than 1% of the O$_2^+$ rate. On the other hand, we find that the ions with a mass from 28 to 30 AMU, which were previously unknown in the Martian ion escape, are an important part of the ionospheric outflow, with a mean escape rate that reaches 32% of the O$_2^+$ rate.

1. Introduction

Mars has only a tenuous atmosphere, with an average surface pressure of roughly 6 mbar. This is believed to have been very different in the past. There is evidence that liquid water flowed on the surface (Baker, 2001), which would require a much denser atmosphere. This would mean that Mars has lost large quantities of its atmospheric content. Estimates of this loss range from less than 150 mbar to several bar (see e.g., Brain & Jakosky, 1998; Jakosky, 2019; Lammer et al., 2013). Likely a large fraction of that has escaped to space. Through neutral and ionospheric escape, a number of processes exist which contribute to this atmospheric erosion (see e.g., Dubinin et al., 2011; Lillis et al., 2017).

The main constituent of the Martian atmosphere is CO$_2$. In the ionosphere, however, O$_2^+$ is the dominant ion. In the dayside ionosphere below roughly 220 km altitude, CO$_2^+$ is the second most abundant ion. This quickly changes toward higher altitudes, however, as the CO$_2^+$ density rapidly decreases with altitude, as opposed to the O$^+$ density which increases until it reaches a peak higher up. At higher altitudes, therefore, the ionosphere is mostly made up of O$_2^+$ and O$^+$ ions. There are a variety of other ions species present in the ionosphere, like HNO$^+$, CO$^+$, HCO$^+$, HO$_2^+$, N$_2^+$, NO$^+$, and so on, which have been observed in situ and are predicted by models (see e.g., Benna et al., 2015; Fox, 2015; Krasnopolsky, 2002; Matta et al., 2014; Withers et al., 2015). Their densities at low altitudes in the dayside ionosphere are very low compared to O$_2^+$, but some of these minor ions become more important at higher altitudes. Moreover, it has been observed that some of them also make up a larger fraction of the nightside ionosphere (Girazian, Mahaffy, Lillis, Benna, Elrod, Fowler, et al., 2017; Girazian, Mahaffy, Lillis, Benna, Elrod, Jakosky, 2017).

The total ion escape and the escape of O$^+$ and O$_2^+$ ions from the ionosphere of Mars has been well studied (see e.g., Barabash et al., 2007; Brain et al., 2015; Dubinin et al., 2017; Fränz et al., 2015; Inui et al., 2019; Lundin et al., 1990; Lundin et al., 2009; Nilsson et al., 2011; Ramstad et al., 2013; Rojas-Castillo et al., 2018; Verigin et al., 1991). Compared to this, only three studies reported on observations of CO$_2^+$ outflow, and no study on any heavy (Atomic Mass Unit [AMU] > 8) ion species other than those three. This is a consequence of the spread in the mass spectrograms of the plasma instruments onboard space missions, which becomes progressively worse for higher masses, and of the high abundances of O$_2^+$ and O$^+$ relative to the other ions. As a result, the major ions obscure the minor ions’ contributions.
Carlsson et al. (2006) and Nilsson et al. (2011) estimated CO$_2$ outflow by fitting peaks in the spectrograms of the Ion Mass Analyzer (IMA) of the ASPERA-3 instrument suite onboard Mars Express. They found high outflowing CO$_2$ fluxes, on average 0.18 and 0.33 of the O$_2$ flux, respectively. Nilsson et al. (2011), however, noted that their method (the same as the one used in Carlsson et al., 2006) most likely overestimated the CO$_2$ abundance. A follow-up study even concluded that most of the time it may be very difficult to get accurate CO$_2$ estimates from the IMA spectrograms (Rojas-Castillo et al., 2018). A study with data from SupraThermal and Thermal Ion Composition (STATIC) onboard Mars Atmosphere and Volatile EvolutioN (MAVEN) reported ratio of CO$_2$ over O$_2$ of 5.9% (Inui et al., 2019), using a method described in (Inui et al., 2019).

In this study we will also use STATIC data to analyze escaping CO$_2$ ions. We will, however, employ a very different method than the one used in Inui et al. (2018, 2019). Moreover, our method will also allow us to investigate some other minor ions which may become important for the ion outflow. In Section 2, we describe the data used, and we explain our method in Section 3. To keep the text succinct, some of the details are described in the Methodological Supplement in the Supporting Information S1. In Section 4, we show the results of our method and analysis, and we discuss them and give some interpretation in Section 5. Finally we will summarize our main conclusions in Section 6.

2. Instrument and Data

The MAVEN Mission was launched in November 2013 and arrived at Mars in September 2014 (Jakosky et al., 2015). It has an elliptical orbit of approximately 6200 × 150 km, although these altitudes have varied over the course of the mission. MAVEN carries a large suite of instruments, including three which can measure ions. Only two of them can separate the ions’ masses: the Neutral Gas and Ion Mass Spectrometer (NGIMS) (Mahaffy et al., 2015) and the STATIC instrument (McFadden et al., 2015).

Since NGIMS’ ion mode is designed to measure thermal ions in the ionosphere only, we use STATIC data for this study.

2.1. Instrument

The SupraThermal and Thermal Ion Composition instrument onboard MAVEN, is an instrument designed to measure the energy distribution and composition of both the thermal and higher energy ion populations present in the Martian ionosphere and its plasma environments (McFadden et al., 2015). It has a nominal field-of-view (FOV) of 360° × 6° which is extended to a maximum FOV of 360° × 90° using electrostatic deflectors. It has a maximum energy range going from 0.1 to 30 keV, which is sampled by an electrostatic analyzer (ESA). After the ESA, the ions are postaccelerated by a 15 kV potential drop, before they enter the time-of-flight (TOF) analyzer, to separate the ions by mass-per-charge. In the TOF section, the ions hit a first carbon foil, producing secondary electrons collected by a micro channel plate detector (MCP) to trigger the start time, after which the ions cross a 2 cm gap to hit the second carbon foil, where again the electron emission triggers the stop time. A final MCP registers the azimuthal angular section. The base time resolution for a complete energy and angular sweep is 4 s. Since STATIC measures mass-per-charge, we will refer to the measured masses in AMU/z, where z is the charge number of the ion. However, since, apart from He$^+$ in the solar wind, we do not expect any significant abundances of ions with a higher charge number than one in the environment of Mars, this is in most cases equivalent to AMU.

To avoid saturation due to a high incoming particle flux, the instrument has both an electrical and a mechanical attenuator, effectively increasing its dynamical range. STATIC also has several modes of operation to maximize its resolution to the plasma environment. Originally, there were four modes which are relevant for our study: the “ram” mode (1), the “conic” mode (2), and the “pickup” (3) and “scan” (4) modes which have an energy range going up to 50,500, and 30,000 eV, respectively, and are used for observations from lower to higher altitudes (the pickup and scan modes have no difference relevant for the data used here). The ram mode has a FOV of 360° × 45°, due to the deflector sweeping a smaller angular range. There is also a “protection” mode (6), during which no energies below 25 eV are sampled. Later during the mission an additional mode (7) was introduced with an energy range from 1–10 eV, such that it has a higher energy resolution near the ram energy at low altitudes in the ionosphere.
STATIC is located on the Articulated Payload Platform (APP), which extends 2 m away from the main spacecraft, allowing STATIC (and the other instruments on the APP) to be oriented independently from the spacecraft orientation. This allows STATIC’s FOV to be directed toward the ram direction at low altitudes in the ionosphere and in the optimal direction to detect pickup ions at high altitudes.

2.2. Data

Because STATIC measures the ions in a four-dimensional parameter space (energy, mass, and angular directions) every 4 s, the full data produced by the instrument is too large for the data transmission limits. Therefore, the data is downsampled and several different data products, representing different cross-sections of the parameter space, are downlinked. In this study we use the “C6” data product, which has the highest mass resolution of all data products that are continuously collected, with 64 mass channels, and 32 energy channels but no angular resolution.

Despite STATIC making measurements since October 2014, in this study we use data collected between February 6, 2016 and May 2019, because before this period the anode rejection (onboard processing to eliminate events with start and stop locations that do not match) was not correctly calibrated, leading to a loss in sensitivity. Measurements from the “protect” mode (mode number 6) are discarded, since in this mode only energies above ∼25 eV are measured. Further details of data selection are given in the Methodological Supplement.

In this study we work with the differential energy flux \( F_E \). Because the full spectrum of 1024 TOF bins is downsampled onboard to 64 mass bins with a different amount of TOF bins per mass bin, we have to divide \( F_E \) by the amount of TOF bins in each specific mass bin to get a flux spectrum as a function of TOF. We will refer to this value as \( F_E^* \).

3. Method

The difficulty in getting the \( \text{CO}_2^+ \) population in the mass spectrogram of a TOF spectrometer stems from the fact that the ions lose energy when hitting the carbon foil that produces the start signal. The amount of energy lost is random, leading to a spread of energy of the ions entering the TOF section. Additionally, the scattering will also lead to a dispersion in the traveling direction of the ions, effectively lengthening distance to be traveled between both carbon foils for some ions. Many more processes, like the dispersion in the TOF of the secondary electrons, may play a role. All these factors lead to a spread in time-of-flight for ions of the same mass-per-charge which is large enough that the distributions of different ion species, with different masses, can overlap. This is worse for larger masses. Since \( \text{O}_2^+ \) is the dominant ion in the Martian ionosphere, it is difficult to extract the \( \text{CO}_2^+ \) contribution, even when it is a significant fraction of the \( \text{O}_2^+ \). In order to separate the different ion species and estimate the contribution by each of these, we will assume a functional form for the distribution in the time-of-flight spectrum of a single ion species, which we then optimize using a least squares minimization method. The moment calculation is performed according to Fränz et al. (2006) and explained in more detail in the Methodological Supplement, and a correction for the spacecraft potential is applied as described in Lavraud and Larson (2016).

3.1. The Time-of-Flight Distribution

The scattering in the carbon foil is a stochastic process which should result in a velocity distribution limited by a maximum and a minimum value (e.g., Allegrini et al., 2006, 2016; Gershman, 2012). As mentioned earlier, there are multiple factors which can cause a spread in time-of-flight. The multiplicative nature of all these factors means that the multiplicative central limit theorem suggests the distribution tends toward a lognormal distribution (Limpert & Stahel, 2017). Ultimately, regardless of theoretical justifications, any functional form has to be validated empirically, and a lognormal distribution turns out to work very well for the STATIC TOF-spectrum.

Therefore, we use a lognormal distribution as the model to fit the ion populations in the time-of-flight spectrum. This function has four parameters \( (I_0, l_{\text{lim}}, \sigma, \mu) \)—their meaning is explained in the Methodological Supplement—which need to be determined, three of which depend on the specific ion species:
Analysis shows that the statistical variation of the O\textsuperscript{2+} distribution due to count statistics may be comparable to the CO\textsubscript{2+} contribution when densities are low and the CO\textsubscript{2+} is a small fraction of the O\textsuperscript{2+}. Therefore, in order to avoid counting the statistical O\textsuperscript{2+} variation as CO\textsubscript{2+}, it is necessary to also fit the CO\textsubscript{2+} distribution, as done in panels (e) and (f) of Figure 1, the fit works very well. It even improves the fit at times-of-flight beyond the peak.

Therefore, in order to represent them with a single distribution, this may add a considerable amount of variation as the distributions due to count statistics may be comparable. Nor can they be explained by O\textsuperscript{+} ions. Distributions are enough to explain the TOF spectrogram taken at 173 km altitude in the dayside ionosphere. In panels c and d, on the other hand, one can see that even including the O\textsuperscript{+} distribution is not enough and more distributions seem to be necessary. This is shown in Figure 1. In panel a and b, the O\textsuperscript{2+} and CO\textsubscript{2+} distributions are enough to explain the TOF spectrogram taken at 173 km altitude in the dayside ionosphere. In panels c and d, on the other hand, one can see that even including the O\textsuperscript{+} distribution is not enough to explain the whole spectrogram, taken at at 244 km altitude. Here, there are counts which cannot be explained by O\textsuperscript{2+} ions because they occur at a time shorter than t\textsubscript{SO2}, the minimum time-of-flight for O\textsuperscript{2+}, or too close to it and thus are too high already for the O\textsuperscript{2+} distribution. Nor can they be explained by O\textsuperscript{+} ions. However, when we add an extra distribution at slightly shorter times-of-flight than O\textsuperscript{2+}, as done in panels (e) and (f) of Figure 1, the fit works very well. It even improves the fit at times-of-flight beyond the CO\textsubscript{2+} peak.

This may seem surprising at first, but other observations of the Martian ionosphere have shown that there are several minor ion species with a mass close to the mass of O\textsuperscript{2+} (Benna et al., 2015; Girazian, Mahaffy, Lillis, Benna, Elrod, Fowler, et al., 2017; Girazian, Mahaffy, Lillis, Benna, Elrod, & Jakosky, 2017; Withers et al., 2015), which is approximately 32 AMU/z. On the dayside at low altitudes in the ionosphere, they constitute but a small fraction. However, on the nightside and at higher altitudes they become more important. While all ion species decrease in density from the dayside to the nightside, some of these minor ions do so at a slower rate than O\textsuperscript{2+}, so that relatively they become more important (Girazian, Mahaffy, Lillis, Benna, Elrod, Fowler, et al., 2017; Girazian, Mahaffy, Lillis, Benna, Elrod, & Jakosky, 2017). As such they may become important enough to affect our analysis.

There is a wide variety of possible candidates for these ions: CO\textsuperscript{+} and N\textsubscript{2+} at 28 AMU/z, HCO\textsuperscript{+} at 29 AMU/z, NO\textsuperscript{+} at 30 AMU/z, HNO\textsuperscript{+} at 31 AMU/z (see e.g., Fox, 2015), and possibly more. Most likely, following other observations, the extra population we observe is a combination of several of these ion species. However, because their mass is so close to the mass of O\textsuperscript{2+}, it may not be possible to resolve all these species separately. Therefore, we decide to represent them with a single distribution. This may add a considerable amount of
uncertainty to our results, but we believe that this is at the limit of what we can resolve with STATIC. When comparing with NGIMS densities, the best agreement is found when summing ions with masses from 28 to 30 AMU/z, therefore we will assume that this population represents ions from that mass range. In the rest of this paper, we will refer to these ions simply as the “NCO-group”, referring to the main atomic constituents (mass-wise) of the molecular ions in this distribution.

4. Results

Figure 2 shows the ion densities calculated using our method for a single ionospheric pass. Lower in the ionosphere, NGIMS can also measure ion densities and composition. Therefore, we can compare them with our calculated STATIC densities. The middle panel shows the densities for $\text{O}^+$, $\text{O}_2^+$, and $\text{CO}_2^+$ distributions are fitted. In panels (e) and (f) an additional distribution for the NCO-group ions is fitted. The top panels (a, c, and e) show the differential flux in a linear scale, whereas on the bottom panels (b, d, and f) on logarithmic scale. The differential energy flux shown divided by the number of TOF-bins per mass bin, to account for the different amount of TOF bins per mass bin. TOF, time-of-flight.

Figure 1. Panel (a) and (b) show the TOF-spectrum fitting for a typical case at low altitudes in the dayside ionosphere, where two populations suffice. Panels (c–f) show a case were additional populations are present. In panels (c) and (d) only the $\text{O}^+$, $\text{O}_2^+$, and $\text{CO}_2^+$ distributions are fitted. In panels (e) and (f) an additional distribution for the NCO-group ions is fitted. The top panels (a, c, and e) show the differential flux in a linear scale, whereas on the bottom panels (b, d, and f) on logarithmic scale. The differential energy flux shown divided by the number of TOF-bins per mass bin, to account for the different amount of TOF bins per mass bin. TOF, time-of-flight.
CO$_2$/$O_2^+$ and NCO-group/$O_2^+$ density ratios are shown in dark blue and dark green, respectively, and for NGIMS in light blue and light green, respectively. Low in the dense ionosphere, both the ratio for CO$_2$ and for the NCO-group give a very similar value for both instruments. The dip in CO$_2$ is also here present in both NGIMS and STATIC data, as is a slight peak in the NCO-group/$O_2^+$ ratio at the same time. At higher altitudes on the inbound leg, the value of the NCO-group ratio seems to differ more between both instruments, but the qualitative behavior still agrees. On the outbound leg, around approximately 15:14 UT, the ions come in from a different direction than the ram direction. As a result, these ions are out of the FOV of NGIMS, and the densities from NGIMS are much lower than those of STATIC, leading to incorrectly high ratios.

There are a multitude of reasons why the absolute densities from STATIC and NGIMS can differ, like their different FOV, spacecraft potential issues, higher temperatures, moving plasma, and so on. Moreover, the calibration of the NGIMS ion sensitivity was performed early in the mission (Mahaffy & Elrod, 2015) and may have changed since, and the STATIC calibration for the absolute densities is not yet finalized and may as of yet only be good to within a factor of 2 (McFadden, 2020).

4.1. Density Altitude Profile

In Figure 3 the median altitude profiles of the ion densities are shown for both STATIC (solid lines) and NGIMS (dashed lines). The O$^+$ density is not shown for STATIC below 200 km altitude, since, as explained in the Methodological Supplement, at those altitudes it is not reliably determined by our method. In the dayside ionosphere (solar zenith angle <90°), shown in the left hand panel, CO$_2$ is the second most abundant...
ion species at low altitudes after $O^+$. The $CO^+_2$ density rapidly decreases with altitude, more rapidly than the other ions, such that the NCO-group density overtakes the $CO^+_2$ already at $\sim$212 km altitude. It is important to remember, of course, that the “NCO-group” ions are most likely the sum of several ion species. The $O^+$ density is very low at the lowest altitudes but increases with altitude and overtakes the $CO^+_2$ density at $\sim$222 km altitude. It becomes the second most abundant species at $\sim$234 km, and its density peaks at $\sim$245 km altitude, after which it slowly starts to decrease.

The nightside altitude profile (solar zenith angle >100°), in the right panel of Figure 3, is quite different from the dayside. The density is lower for all ion species, as is expected, but the composition is also drastically different. Particularly the $CO^+_2$ fraction is much lower, with its median density at no altitude reaching more than 0.05 of the $O^+_2$ density, compared to 0.15–0.20 on the dayside. On the other hand, the NCO-group becomes much more important on the nightside, and are, as a group, by far the second most abundant species. Their density is around 0.2 of the $O^+_2$ density at low altitudes in the nightside ionosphere, and this fraction increases with the altitude. The $CO^+_2$ density decreases strongly with altitude from $\sim$175 km on. The $O^+_2$ and NCO-group densities do so as well below 200 km, but above that point, the decrease lessens and becomes very small from 350 km altitude on. The $O^+$ density is already higher than the $CO^+_2$ density at 200 km and seems to decrease barely. Around $\sim$400 km altitude it becomes more abundant than the NCO-group ions.

The absolute densities in the dayside profiles do not agree exactly between STATIC and NGIMS, but they are of the same order. Qualitatively, however, they agree very well, as is evidenced by the fact that the qualitative description of the STATIC dayside profile, given higher up, applies equally well to the NGIMS profile (with the exception of the cross-over altitudes which are all roughly 18 km lower for NGIMS, and the $O^+$ peak altitude which is 4 km lower). For the nightside this is different. Whereas at low altitudes the densities agree somewhat qualitatively, from 200 km altitude on the NGIMS densities decrease more rapidly than the STATIC densities. It is difficult to speculate on the cause of this discrepancy. However, one possibility may be that the plasma on the Martian nightside starts to move at lower altitudes than on the dayside, so that it deviates from the static, thermal plasma at low altitudes in the ionosphere, for which NGIMS is designed, and so that the FOV becomes more important.

4.2. $CO^+_2$ Throughout the Martian Magnetosphere

$CO^+_2$ ions are observed practically everywhere throughout the induced magnetosphere of Mars, although they are far from observed all the time. Figure 4a shows the spatial variation of the rate at which $CO^+_2$ is observed in 500-by-500 km bins in the $x_{MSO}$ and $R_{MSO}$ directions (where $R_{MSO} = \sqrt{x_{MSO}^2 + z_{MSO}^2}$). At low alti-
In the dayside ionosphere, we find a CO$_2^+$ population almost all the time (>97% of the time), and even in the nightside ionosphere we detect it the majority of the time (~75% of the time). Further downstream in the magnetotail, however, CO$_2^+$ ions are found much less regularly, only roughly 20% of the time. Note that it is in many cases impossible to say whether a measurement with no CO$_2^+$ really means the absence of CO$_2^+$ or whether its population is merely too tenuous compared to the O$_2^+$ population to be distinguished from it. This means that calculating average CO$_2^+$ densities and fluxes at high altitudes is not a statistically trivial task, and motivates our methods explained in Section 2 of the Methodological Supplement. We will explore

Figure 4. (a) The spatial distribution of the rate at which CO$_2^+$ is observed throughout the Martian space environment. (b) The spatial distribution of the CO$_2^+$ density. Both panels with STATIC data from February 2016 to May 2019. STATIC, SupraThermal and Thermal Ion Composition.
this further in Section 4.5. Outside of the pile-up boundary layer the observation rate of (low-energy) CO\textsubscript{2}\textsuperscript{+}
quickly decreases, as one would expect.

The mean CO\textsubscript{2}\textsuperscript{+} density, in Figure 4b, reveals a similar picture, although the drop across the terminator is much stronger: from dayside to nightside the density drops roughly three orders of magnitude. Beyond the pile-up boundary layer, the CO\textsubscript{2}\textsuperscript{+} density falls off sharply and quickly reaches values of the order of 10\textsuperscript{-3} cm\textsuperscript{-3} or lower and keeps decreasing with radial distance. The observations of CO\textsubscript{2}\textsuperscript{+} further out in this region are typically the low-energy tail of pickup ion distributions. Since we restrict our observations to energies below 100 eV we exclude the major part of these distributions. But the observed density may often also be an effect of the noise mentioned in Section 3 of the Methodological Supplement. It is difficult to say which cause has the largest effect on the mean density, so values in this region need to be taken with caution. The mean density in the magnetotail is also very low, but markedly higher than outside of the induced magnetosphere: typically on the order of 10\textsuperscript{-3} cm\textsuperscript{-3}, but decreasing gradually with −x\textsubscript{MSO}. Another distinct feature visible in Figure 4b near the “low-SZA nightside” (i.e., in the nightside but at SZAs smaller than 150\degree) is a “bulge” of slightly higher density CO\textsubscript{2}\textsuperscript{+} than in the rest of the tail, with densities being on the order of 10\textsuperscript{-1} cm\textsuperscript{-3} (roughly located between R\textsubscript{cyl} = 1,500 km and R\textsubscript{cyl} = 4,000 km and extending until x\textsubscript{MSO} = −5,000 km or −5,500 km, the feature is more clearly visible in Figure 7, which is discussed later).

The O\textsubscript{2}\textsuperscript{+} density, presented in Figure 5a, also drops from dayside to nightside, but not as strongly as the CO\textsubscript{2}\textsuperscript{+} . The dayside O\textsubscript{2}\textsuperscript{+} is between 10 and 100 times more dense than on the nightside. The O\textsubscript{2}\textsuperscript{+} density in the magnetotail is on the order of 1–10 cm\textsuperscript{-3} and seems to be slightly higher within the optical shadow of the planet than in the outer tail. The denser bulge seems much less distinct than for CO\textsubscript{2}\textsuperscript{+}. The NCO-group density, in Figure 5b, is much lower in the dayside ionosphere than the O\textsubscript{2}\textsuperscript{+}, but it falls off much less strong toward the nightside. Higher up, the NCO-group density exhibits the same features as O\textsubscript{2}\textsuperscript{+}, and the densities become more comparable, despite the NCO-group still being significantly less dense. Its values in the tail are roughly of the order of 1 cm\textsuperscript{-3}, but decrease gradually with −x\textsubscript{MSO}, as does the O\textsubscript{2}\textsuperscript{+} density.

### 4.3. Composition

To analyze the changes in composition, we compare the CO\textsubscript{2}\textsuperscript{+} and NCO-group densities to the O\textsubscript{2}\textsuperscript{+} density. The spatial map of the CO\textsubscript{2}\textsuperscript{+} over O\textsubscript{2}\textsuperscript{+} density ratio is shown in Figure 6a. Note that we have chosen to present the ratio of the (spatial) averages rather than the average of the ratios (since the arithmetic mean is not an appropriate statistic for ratios, but there is no good other option due to the large amount of zero values). We also removed any bins that had less than 20 measurements on separate orbits with a high enough fit quality (SAE ≤ 0.2, see Methodological Supplement Section 2). It is clear that, as mentioned before, the CO\textsubscript{2}\textsuperscript{+} drops faster than the O\textsubscript{2}\textsuperscript{+} density across the terminator. On the dayside the CO\textsubscript{2}\textsuperscript{+} is between 20% and 30% of the O\textsubscript{2}\textsuperscript{+} density, whereas on the nightside this is only 5% or less. The importance of CO\textsubscript{2}\textsuperscript{+} in the composition clearly decreases with altitude. The high density bulge is also here visible, however, less distinctly than in the CO\textsubscript{2}\textsuperscript{+} density. This suggest that it is also there for O\textsubscript{2}\textsuperscript{+}, but to a lesser extent. Its ratio varies from 1%–3%. In the center of the tail, the mean CO\textsubscript{2}\textsuperscript{+} rapidly drops below 1% of the O\textsubscript{2}\textsuperscript{+}. In the outer part of the tail, the ratio seems to be slightly higher and hovers around 1%.

The ratio of the NCO-group over the O\textsubscript{2}\textsuperscript{+} is shown Figure 6b. Note that a very different, and linear, color scale is used here and in Figure 6c from the one in Figure 6a (which is logarithmic). In the dayside ionosphere, the NCO-group ions are mostly below 10% of the O\textsubscript{2}\textsuperscript{+} density. In the nightside ionosphere the NCO-group becomes more important as their ratio rises to 15%–25%. In the magnetotail the fraction of the NCO-group varies rather little, being almost everywhere between 25% and 35%.

Both CO\textsubscript{2}\textsuperscript{+} and the NCO-group exhibit relatively high ratios over O\textsubscript{2}\textsuperscript{+} in the magnetosheath. It is difficult to say whether this is a real physical effect or an artifact resulting from the noise described in the Methodological Supplement. The latter is more probable, considering that this noise leads to an overestimation of both the NCO-group and the CO\textsubscript{2}\textsuperscript{+} density but not the O\textsubscript{2}\textsuperscript{+} density.

The O\textsuperscript{+} over O\textsubscript{2}\textsuperscript{+} ratio, shown in Figure 6c, is small in the ionospheric bins, since at very low altitudes in the ionosphere, O\textsuperscript{+} has the lowest density of all the ions species discussed here (remembering that the “NCO-
group” species most likely is the sum of multiple different ion species). However, its density quickly increases with altitude, overtaking the NCO-group and becoming roughly ~1.5–2.5 times more abundant than them. O\textsuperscript{+} remains nonetheless the most important ion species almost everywhere as the mean O\textsuperscript{+} density reaches only ~0.5–0.65 of the O\textsuperscript{2+} in the magnetotail.

4.4. Fluxes

The fluxes behave very similarly to the densities, but still there are some slight differences. Visually these are rather difficult to distinguish in the spatial maps. Therefore, it is more informative to look at the ratio of the spatial means of the flux and the density, shown in Figure 7a for CO\textsuperscript{2+} in km s\textsuperscript{-1}. The ratio of flux and density can be interpreted as the magnitude of the velocity, although caution is necessary, since we present the ratio of the spatial averages rather than the average of the ratios. Moreover, we did not subtract the spacecraft velocity, which means it is the velocity in the frame of the spacecraft, nor did we take into account the direction of observation (since there is no STATIC data product with both a high enough mass resolution and directional information).

Figure 7a shows that, as expected, the mean ratio of flux and density at low altitudes in the ionosphere is small and roughly equals the mean spacecraft velocity. Higher up, however, the ratio is no longer determined by the spacecraft velocity, meaning that the plasma is moving. At the area where the high density bulge is observed in Figure 4b, the flux-density ratio seems to be particularly low, compared to in the rest of the tail, which may suggest low mean CO\textsuperscript{2+} velocities. The same feature, but much less distinct, can be seen in the O\textsuperscript{2+} flux-density ratio in Figure 7b. The NCO-group flux-density ratio (not shown) looks similar to that of O\textsuperscript{2+}, except being slightly higher and having an even less distinct bulge. For all species, however, the flux-density ratio increases in the \(\sim x_{\text{MSO}}\) direction, suggesting that the plasma in the tail is accelerated in the antisunward direction. This was also reported by other studies (see e.g., Inui et al., 2019).

4.5. Escape Rates

From the mean fluxes we can calculate a total escape rate through the tail, if we assume that at a certain distance all observed ions are escaping and moving in the \(\sim x_{\text{MSO}}\) direction, say from \(-5,500\) km. We multiply the mean flux in each bin (at \(x_{\text{MSO}} = -5,500\) km) with its surface area. Doing this for CO\textsuperscript{2+} yields an escape rate of 1.3 \times 10^{22} ions s\textsuperscript{-1}, compared to an escape rate of 1.8 \times 10^{24} s\textsuperscript{-1} for O\textsuperscript{2+}. The NCO-group ions are found to escape at 5.8 \times 10^{23} s\textsuperscript{-1}, and the O\textsuperscript{+} ions at 1.3 \times 10^{24} s\textsuperscript{-1}. The CO\textsuperscript{2+} escape is much lower than that of the O\textsuperscript{2+}, and represents only 0.72% of the latter. The NCO-group, on the other hand, represents a significant fraction of the outflowing ions and amount to 32% of the O\textsuperscript{2+}. The O\textsuperscript{+} ions reach 71% of the O\textsuperscript{2+}. These ratios remain roughly constant from \(x_{\text{MSO}} = -5,000\) km on, meaning that the composition of the (heavy) outflowing ions (with energy below 100 eV) does not change anymore beyond that point. The total heavy ion escape rate amounts to 3.7 \times 10^{24} s\textsuperscript{-1}.

As highlighted by Figure 4a, however, outside of the ionosphere, the majority of the time either the CO\textsuperscript{2+} fraction is too small to be detectable or there is no CO\textsuperscript{2+} present. As a result, the escape rate calculated for CO\textsuperscript{2+} (as well as the mean densities, fluxes, and ratios given earlier on) are affected by the choices of how to deal with these nondetections. If one were to discard all these measurements with zero CO\textsuperscript{2+}, the average escape rate would go up to 1.1 \times 10^{24} s\textsuperscript{-1} however, this would be an artificial increase since it ignores all the datapoints where CO\textsuperscript{2+} was either absent or too tenuous to measure.

We can estimate a 95% confidence interval for the total CO\textsuperscript{2+} outflow, by combining the standard error from the linear least squares estimation on each datapoint and the statistical uncertainty on the mean due to the natural variation (we sum the uncertainty of each bin). For the error from the fitting, every measurement can be considered an independent measurement. For the statistical variation this is not true, since we use a moving mean of 64s (17 datapoints), and measurements may be auto-correlated. In order to avoid this issue, we count every separate orbit as a an individual measurement. This most likely overestimates the error. The resulting confidence interval is [0.835, 1.76] \times 10^{22} s\textsuperscript{-1} for CO\textsuperscript{2+}. Applying the same method for O\textsuperscript{2+} gives [1.49, 2.12] \times 10^{24} s\textsuperscript{-1}, for the NCO-group [4.75, 6.86] \times 10^{23} s\textsuperscript{-1}, and for O\textsuperscript{+} [1.05, 1.52] \times 10^{24} s\textsuperscript{-1}. The uncertainty due to the statistical variation is for all ion species much larger than the uncertainty due to the fitting.

To check the validity of our assumption that all ions observed at \(x_{\text{MSO}} = -5,500\) km escape, we can perform this calculation at several tailward distances. Beyond \(x_{\text{MSO}} = -6,500\) this may become problematic and the
uncertainty is much higher, because spatial coverage in the tail and the number of measurements decreases drastically. We also have to use an average flux for the missing bins (but we do not integrate beyond the $R_{cyl} = 7,000$ km bin, since the flux is not uniform across $R_{cyl}$). The resulting escape rates are shown in Figure 8. We see that from $x_{MSO} = -5,500$ the escape rate does not vary significantly anymore, and any variation until $x_{MSO} = -7,000$ is well within the confidence intervals given earlier. Even further down the tail, the escape rates are very reasonable, despite the aforementioned issues.

Figure 5. (a) The spatial distribution of the $O_2^+$ density. (b) The spatial distribution of the NCO-group density. Both panels with STATIC data from February 2016 to May 2019. STATIC, SupraThermal and Thermal Ion Composition.
Figure 6. (a) The spatial distribution of the CO$^+_2$ over O$^+_2$ density ratio. (b) The spatial distribution of the NCO-group over O$^+_2$ density ratio. (c) The spatial distribution of the O$^+$ over O$^+_2$ density ratio. Note the different color scale for panel (a). All panels with STATIC data from January 2016 to May 2019. STATIC, SupraThermal and Thermal Ion Composition.
5. Discussion

As Figure 4b shows, low energy (<100 eV) CO$_2$ ions can be observed flowing throughout the Martian induced magnetosphere. Very often, though, CO$_2$ is either absent or too tenuous to be measured outside of the ionosphere. As already mentioned in Section 4.5, this needs to be taken into account, when interpreting the CO$_2$ results. Nonetheless, it is clear that CO$_2$ is escaping at a rate with an order of magnitude
of $10^{22}$ ions s$^{-1}$. This is much less than the escaping $O_2^+$, only 1% or less. Though, there may be some uncertainty on this number, the average $CO_2^+$ in the escaping ions certainly does not reach more than a few percent of the $O_2^+$. This may be understandable looking at Figure 3, which shows that the $CO_2^+$ density drops to 1% or even less of the $O_2^+$ density at higher altitudes.

In the densities of $O_2^+$ and the NCO-group in Figures 5a and 5b, one can see a sudden drop in the tail at $R_{cy} = 3,500$ km. $2CO^+$ seems to be less affected by this. This is near the boundary of Mars’ optical shadow and thus most likely an effect of the spacecraft potential. In the optical shadow, a spacecraft can get charged negatively leading to wrong estimates of the moments. We correct for this in the moment calculation using estimates of the negative spacecraft potentials determined by the STATIC instrument team. Outside of the optical shadow, on the other hand, EUV radiation may cause a positive spacecraft potential if the plasma density is very low, leading to an underestimation of the density or even blocking low-energy ions from reaching the detector.

Apart from this sudden drop, the density decreases gradually toward the outside of the tail. This is also the case for the flux. This decrease is stronger than the increase in surface area for the cylindrical shells. The optical shadow region therefore accounts for already more than half of the total escape, despite comprising only a fourth of the surface area of the whole tail (at $\sim x_{MSO} = -5,500$ km). The regions just outside the optical shadow are also important for the total escape, but further out the contribution becomes progressively smaller, despite the increased surface area.

5.1. The NCO-Group

Figures 5b and 6b show an important result. A significant proportion of the (heavy) ionospheric outflow, roughly 16%, is supplied by ions with a mass between 28 and 30 AMU/z (or perhaps 31 AMU/z), which we called the NCO-group. These ions also reach about a third of the $O_2^+$ abundance, and thus represent roughly a quarter of the ions with a mass near 30 AMU/z. This also means that about a quarter of the outflowing ions which may often be counted as $O_2^+$ ions are actually a different (or multiple different) ion species with a slightly lower mass. Potential candidates for these ion species with a mass of 28–30 AMU/z (or perhaps 31 AMU/z) are $CO^+$, $N_2^+$, $HCO^+$, $NO^+$ (and perhaps $HNO^+$) (Fox, 2015), and possibly more.

Despite being a significant fraction of the outflowing heavy ions, the NCO-group ions seem to not have been considered in any other study about ionospheric outflow from Mars. This is understandable, since their mass is so close to that of $O_2^+$, the most abundant ion in both the Martian ionosphere and its outflow, and each of these ion species at low altitudes in the ionosphere separately barely reaches a few percent of the $O_2$ density (Benna et al., 2015). However, in hindsight their significance in the outflowing ion composition may not surprise us: combined, these ions’ density quickly gains in importance with altitude in both observations and models (see e.g., Benna et al., 2015; Fox, 2015; Girazian, Mahaffy, Lillis, Benna, Elrod, Fowler, et al., 2017; Girazian, Mahaffy, Lillis, Benna, Elrod, & Jakosky, 2017; Krasnopolsky, 2002; Matta et al., 2014; Terada et al., 2009; Withers et al., 2015).

These ions of the NCO-group may also be an important component in the atmospheric erosion on Mars. $CO_2^+$—despite being the result of the photo-ionization of the most abundant constituent of the Martian atmosphere—is rather underrepresented in the ionospheric escape. For Jeans escape the $CO_2$ molecule is too heavy. Modeling suggests that sputtering due to precipitating pickup ions may be more efficient in causing $CO_2$ to escape (Leblanc et al., 2018). However, the NCO-group ions are an even larger and significant part of the escaping ions. Both $CO^+$ and $HCO^+$ are molecular ions containing carbon and oxygen and are the product of (a chain of) chemical reactions of which $CO_2$ is ultimately the origin. Therefore, they present an indirect, but more likely route for $CO_2$ to escape, and thus contribute to the erosion of carbon and $CO_2$ in the Martian atmosphere.
5.2. High-Density Bulge

An interesting feature, most clearly visible in the CO$_2$ in Figure 4b, is the bulge of higher density plasma at the nightside. It is stronger in the density than in the flux, which would suggest that it is related to the ion velocity. It is also stronger for the heavier ions (it is the weakest for O$^+$), which points toward gravity being an important factor. Therefore, one could interpret this as ion-flows originating in the dayside and being transported to the nightside. Transterminator fluxes were observed by Mars Express (Fränz et al., 2010) and are suggested by modeling results (e.g., Chaufray et al., 2014; Cui et al., 2015). When their flow velocity begins to change from horizontal to vertical, gravity will start to act on it, causing the ions to slow down. Some may not have enough energy to escape and become stagnant or even fall back down into the ionosphere, depending on the balance of the forces. This could explain why there is so little CO$_2$ escaping through the tail.

Additionally, if a convection electric field is moving the plasma tailwards, heavier ions will be less strongly magnetized, so that they will be more likely to be slowed down by gravity. It should be mentioned that Wu et al. (2019) argued that the upward force due to the magnetic pressure far outweighs any other force at altitudes above 400 km. Their analysis is only valid for areas with a horizontal magnetic field orientation, however, which may not always be representative of the magnetic topology in the region discussed here. Moreover, the upward velocities and escape rates predicted from their theoretical calculations have not yet been confirmed by observations. Other escape process, like polar wind outflows, may be present (Dubinin et al., 2011), which may depend on mass. A further analysis, using directional data, and looking at the effect of the convection electric field and other solar wind drivers as well ionospheric pressures or temperatures may shed more light on this matter. We leave this for future work.

5.3. Day-to-Night Difference

From Figures 3, 4b, 5a, and 5b, it is clear that the densities of all ion species decrease from dayside to nightside. This is clearly what one would expect, since the main source of ions is photo-ionization by extreme ultra-violet light (EUV), which is absent on the nightside. Figures 6a and 6b, however, show this does not happen equally for all ion species: CO$_2$ density decreases much more than the O$_2$ density, whereas the NCO-group density falls off much less strong. Therefore, also the ionospheric composition changes drastically from dayside to nightside. The same behavior was observed by Girazian, Mahaffy, Lillis, Benna, Elrod, Fowler, et al. (2017) and Girazian, Mahaffy, Lillis, Benna, Elrod, & Jakosky (2017) with the NGIMS ion instrument onboard MAVEN. They found a stronger decrease of CO$_2$ than O$_2$ and a smaller decrease of HCO$^+$ and NO$^+$ (which in our study are summed together in the NCO-group distribution).

A very plausible explanation for this change in composition was given by Girazian, Mahaffy, Lillis, Benna, Elrod, Fowler, et al. (2017) and Girazian, Mahaffy, Lillis, Benna, Elrod, & Jakosky (2017) in terms of ionospheric chemistry. The main source for CO$_2$ is photo-ionization, whereas CO$^+$, HCO$^+$, and NO$^+$ are all products of chemical processes including some in which CO$_2$ and O$_2$ are reactants. Moreover, they suggested CO$_2$ may have a shorter lifetime since it is more likely to decay due to chemical reactions with neutrals. Therefore, whereas there is no EUV on the nightside to replenish the decayed CO$_2$, the ions of the NCO-group are more likely to survive into the night and might even be produced there by the decay of the other ions.

Another possible explanation may be day-to-night transport. If plasma-flows across the terminator, be they driven by pressure gradients or the solar wind, become more important higher up in the ionosphere, less CO$_2$ will be transported toward the nightside (and comparatively more NCO-group ions), since its share in the ionospheric composition rapidly decreases with altitude (and the NCO-group’s increases). Finally, electron precipitation is an important source of ionization in the nightside ionosphere (see e.g., Adams et al., 2018; Cui et al., 2019; Fowler et al., 2015), and this may also affect its composition. However, NGIMS observations seem to suggest this would be more efficient for enhancing CO$_2$ and O$^+$ densities rather than the NCO-group’s densities (Girazian, Mahaffy, Lillis, Benna, Elrod, Fowler, et al., 2017; Girazian, Mahaffy, Lillis, Benna, Elrod, & Jakosky, 2017) (although, of the NCO-group, only NO$^+$ was investigated).
5.4. Other Escape Rates from STATIC Data

Other escape rates with STATIC data have been reported. Brain et al. (2015) found a total ion outflow of $2.8 \times 10^{24} \text{ s}^{-1}$ for heavy ions, which is not much lower than the $3.7 \times 10^{24} \text{ s}^{-1}$ we find, despite that they only looked at ions with energy above $25 \text{ eV}$. We may miss the escape via the ion plume, however, which according to Dong et al. (2015) may contribute roughly $0.5 \times 10^{24} \text{ s}^{-1}$, and other outflowing ions with energies above $100 \text{ eV}$. Additionally, the time period investigated by Brain et al. (2015), November 2014 to April 2015, was near the solar maximum, compared to our time period from January 2016 to May 2019. The same can be said about the tailward O$^+$ escape rates found by Dong et al. (2015), which are similar to, but slightly higher than ours.

Dubinin et al. (2017) reported an O escape rate of $6.2-7.35 \times 10^{24} \text{ s}^{-1}$ which included O$^+$ and O$_2^+$ ions, with data from November 2014 to May 2016. If we assume all ions in the NCO-group contain one O atom (i.e., CO$^+$, HCO$^+$, or NO$^+$), we find a rate of $5.5 \times 10^{24} \text{ s}^{-1}$. If we count the NCO-group as contributing two O atoms (i.e., if one were to count them as O$_2^+$), we find $6.1 \times 10^{24} \text{ s}^{-1}$. Inui et al. (2019) found a (mean) O escape rate of $4.3 \times 10^{24} \text{ s}^{-1}$ (and a median of $2.1 \times 10^{24} \text{ s}^{-1}$) for the optical shadow, with data from July 2015 to December 2017. For the optical shadow we find a mean rate of $2.9$ or $3.2 \times 10^{24} \text{ s}^{-1}$ (respectively, according to the assumptions mentioned before). These differences may well be explained by statistical variation, a time period nearer to the solar maximum, and a different method. The suggestion by Inui et al. (2019) that this value may quadruple when including the whole magnetotail, however, is not born out in our results, although the effect of the spacecraft potential on observed densities needs to be taken into account.

5.5. Other CO$_2$ Observations

Carlsson et al. (2006) studied CO$_2$ in Martian ionospheric outflow using data from the IMA of the ASPERA-3 instrument suite onboard Mars Express. They found a much higher CO$_2$/O$_2$ ratio of 0.18 than in our present study. These results were based on a limited set of 77 selected events with rather high fluxes, mostly in the region of $-x_{MSO}$ from −1.5 to 0 R$_E$ and $R_{sys}$ from 0 to 1 R$_E$. In this region we find slightly higher CO$_2$ over O$_2$ ratios than further downstream, on the order of a few percent, but still much lower than Carlsson et al. (2006). The energies of the ions they looked at, however, ranged from 300 to 3,000 eV, while we only investigated ions with energies up to 100 eV.

A later study with a much larger IMA data set by Nilsson et al. (2011) found an even higher ratio of $\frac{1}{3}$, but also cautioned that a re-analysis of the IMA data suggested that their estimates of CO$_2$, as well as the ones in Carlsson et al. (2006), were likely overestimates. A follow-up study, Rojas-Castillo et al. (2018), concluded that the overlap of the O$_2$ and CO$_2$ distributions in the IMA mass spectrogram is too large to accurately estimate the CO$_2$ population and more work is needed. Indeed the mass resolution of IMA, being an older instrument, is lower (combined with a lower sensitivity and time resolution) than that of STATIC, so that already to separate O$^+$ and O$_2^+$ a peak-fitting method is needed, which may lead to extra uncertainty in the CO$_2$ determination.

Inui et al. (2019) also used STATIC data to look at CO$_2$ and found a CO$_2$/O$_2$ ratio of 5.9% in the outflow in the optical shadow. This is much higher than our results. They do not have an energy limit as we do. However, most likely most of the difference is due to very different method being employed. The method used in (Inui et al., 2019), described in Inui et al. (2018), also assumes a lognormal distribution, but beyond that is completely different from ours. The main differences are that in the Inui et al. (2018) method

1. Only the O$_2$ distribution is fitted, which is then subtracted, after which the residuals are counted as CO$_2$, whereas in our method both O$_2$ and CO$_2$, as well as O$^+$ and the NCO-group are fitted
2. The amplitude $I_{O_2}$ (k in Inui et al., 2018) is not fitted for but fixed to the maximum of the O$_2$ counts, whereas the $I$s (for each distribution) are what is fitted for in our method
3. The parameters $I_{O_2}$, $\sigma_{O_2}$, and $\mu_{O_2}$ are fitted for (c, $\sigma$, and $\mu$, respectively, in Inui et al. (2018)), whereas in our method those nonlinear parameters are determined a priori and kept constant (making it a linear system)
4. The fitting is performed in the mass-per-charge space, whereas in our method this is done in time-of-flight. The reasons for our choices are given in Section 3 and in the Methodological Supplement Section 1. Differences are also likely to arise from different statistical assumptions, as discussed in Section 4.5 and in the Methodological Supplement Section 2.

5.6. Other Minor Ions

As a final note, we should mention that there are several other minor ions species which may be important in the overall outflowing ion composition. They may all make for interesting topics for future studies. We did not discuss H+, which is the dominant component in the ion escape on Venus and Earth due to the higher gravity, nor He+ (or any of hydrogen's molecular variations such as H2 or H3).

Several heavier minor ions may be worth looking at as well. NGIMS observations reveal that, at low altitudes in the ionosphere, C+ and N+ abundances are several orders of magnitudes less than O+ (Benna et al., 2015), which has a similar mass, but that their fraction in the total ion density goes up significantly with altitude. These abundances seem unlikely to reach more than a few percent of the O+ density, but it may still be possible to separate them because of STATIC's higher mass resolution at lower masses and the TOF bins not contaminated by O+.

A possibly more important ion species may be OH+. NGIMS observations indicate that, while being very insignificant at low altitudes in the ionosphere, this molecular ion rapidly gains in importance at higher ionospheric altitudes (Benna et al., 2015; Withers et al., 2015). Around 350 km altitude, it seems to become the third most abundant ion (after O2+ and O+), and is similar in density to the sum of the ions at 28–30 AMU/z. Considering that the latter are a significant part of the ion outflow, OH+ may well be also. Separating this from O+ in the mass spectrogram may prove more challenging, though, since the masses are very close and O+ is both the more abundant and the lighter ion.

Lastly, observations (Benna et al., 2015) and some ionospheric models (see e.g., Fox, 2015; Krasnopolsky, 2002; Matta et al., 2014) suggest HCO+ (sometimes also referred to as OCOH+) may reach a significant fraction of the CO2+ density. However, considering the low density of CO2+ in the ionospheric outflow, the small difference in mass (only 2% of their mass), and the lower mass resolution at these higher masses, it seems unlikely that these ions can be separated in the outflowing ion composition with STATIC data. If OH+ or HCO+ are indeed present in the outflow, they are most likely counted in the O+ and CO2+ distributions.

6. Conclusion

In this study we looked at the composition of the heavy ions escaping from the Martian ionosphere with energies up to 100 eV. In order to do so, we fitted four ion populations to STATIC's mass spectrograms: for O+, for O2+, for CO2+, and one for ions with a mass between 28 and 30 AMU/z. Our results at low altitudes in the ionosphere agree qualitatively very well with NGIMS results. Our main conclusions are as follows:

- CO2 can be observed practically everywhere in the induced magnetosphere of Mars. Downstream in the magnetotail, however, it is detected only 20% of the time
- The density of CO2 ions rapidly decreases with altitude, and they escape only in small amounts. The mean escape rate is 1.3 \times 10^{23} \text{ ions s}^{-1}, and therefore CO2 is a very minor ion in the ionospheric outflow, reaching only 1% or less of the O2+ outflow
- The ions with a mass between 28 and 30 AMU/z make up a significant fraction of the heavy ion outflow (16%) and reach a third of the the O2+ density. They thus represent a quarter of all the ions with mass near 30 AMU/z. This ion population has not been addressed in previous studies about ionospheric escape from Mars

In this study, we did not investigate the effect of the convection electric field or other solar wind drivers on the ion outflow and composition, nor that of variation in ionization due to changes in solar irradiation or...
orbital motion. We also did not look at how the crustal magnetic fields affect all of this. This will be analyzed in future research.

Data Availability Statement
All MAVEN data can be found at https://lasp.colorado.edu/maven/sdc/public/.

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