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### Key Points:

- Analysis of data from the Cassini Plasma Spectrometer confirms negative pickup ions originating from Saturn's moon Dione
- The negative pickup ions are consistent with O<sup>-</sup> originating from Dione's exosphere
- Density estimates indicate that negative pickup ions may represent a significant loss channel for Dione's exosphere

### Correspondence to:

T. A. Nordheim,  
nordheim@jpl.nasa.gov

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## Detection of Negative Pickup Ions at Saturn's Moon Dione

T. A. Nordheim<sup>1</sup> , A. Wellbrock<sup>2,3</sup> , G. H. Jones<sup>2,3</sup> , R. T. Desai<sup>4</sup> , A. J. Coates<sup>2,3</sup> ,  
B. D. Teolis<sup>5</sup> , and J. M. Jasinski<sup>1</sup>

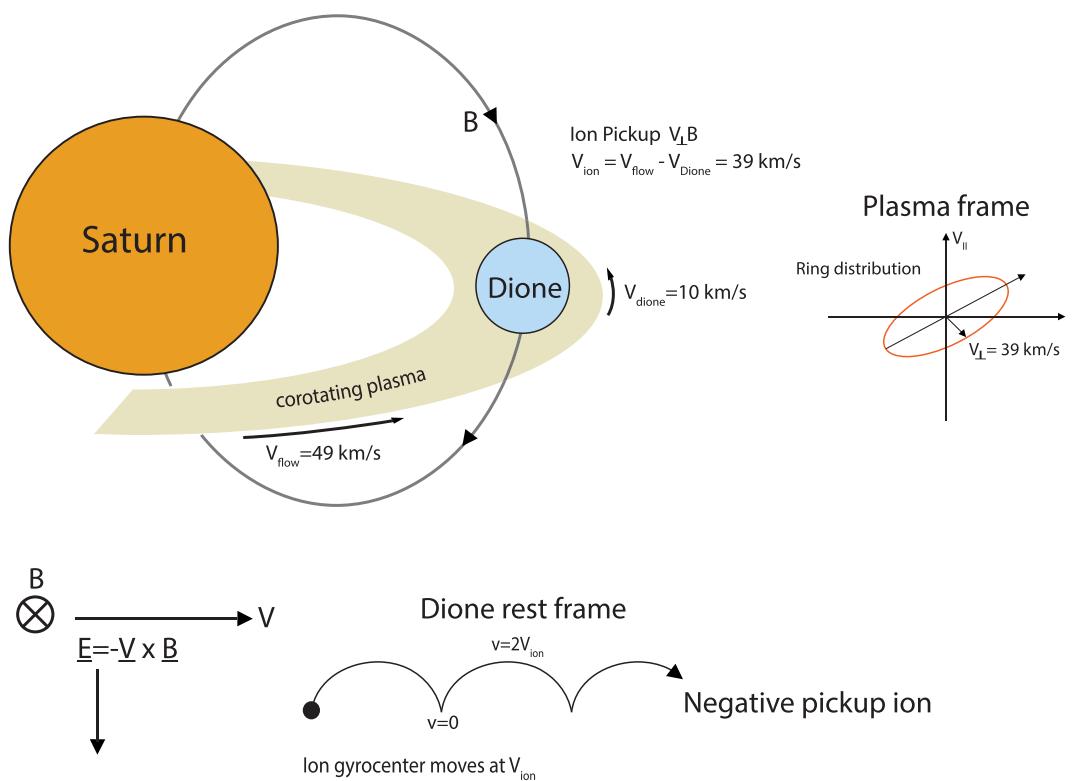
<sup>1</sup>Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA, <sup>2</sup>Mullard Space Science Laboratory, University College London, Dorking, UK, <sup>3</sup>Centre for Planetary Sciences at UCL/Birkbeck, University College London, London, UK, <sup>4</sup>Blackett Laboratory, Imperial College London, London, UK, <sup>5</sup>Division of Space Science and Engineering, Southwest Research Institute, San Antonio, TX, USA

**Abstract** We investigate a possible negative ion feature observed by the Cassini Plasma Spectrometer (CAPS) during a flyby of Saturn's moon Dione that occurred on 7 April 2010. By examining possible particle trajectories, we find that the observed particles are consistent with negative pickup ions originating near the moon's surface. We find that the mass of the negative pickup ions is in the range of 15–25 u and tentatively identify this species as O<sup>-</sup>, likely resulting from ionization and subsequent pickup from Dione's O<sub>2</sub>-CO<sub>2</sub> exosphere. Our estimates show that the negative ion density is  $\sim 3 \times 10^{-3} \text{ cm}^{-3}$ . This is comparable to, but slightly smaller than, that previously reported for the density of O<sub>2</sub><sup>+</sup> pickup ions for the same flyby, indicating that negative pickup ions may represent a major loss channel for Dione's exosphere.

## 1. Introduction

In both dense and tenuous planetary atmospheres, negative ions may be formed by processes such as radiative or dissociative electron attachment and ion pair production (e.g., due to photoionization) (Vuitton et al., 2009). Negative ions have been found within the *D* region of the terrestrial ionosphere (Arnold et al., 1971; Johnson et al., 1958) and have been predicted to occur within the atmospheres of Venus (Borucki et al., 1982; Dubach et al., 1974), Mars (Molina-Cuberos, 2002; Whitten et al., 1971), and Jupiter (Capone et al., 1979). Negative ions have also been observed within the inner coma of comet 1P/Halley (Chaizy et al., 1991) and in the solar wind near the nucleus of comet 67P/Churyumov-Gerasimenko (Burch et al., 2015). During the Cassini Grand Finale, the Langmuir Probe of the Radio Plasma Wave Science (RPWS-LP) instrument observed heavy negative ions within Saturn's ionosphere, indicating that these particles are a major population (Morooka et al., 2019). The Cassini Electron Spectrometer (ELS) (Linder et al., 1998), part of the Cassini Plasma Spectrometer (CAPS) (Young et al., 2004), discovered negative ions within Titan's upper atmosphere (Coates et al., 2007; Desai, Coates, et al., 2017; Waite et al., 2007; Wellbrock et al., 2019). This instrument detected candidate negative ions with masses of up to 13,800 u/q (Coates et al., 2009; Wellbrock et al., 2013). CAPS-ELS also detected negative ion species during several flybys of Enceladus. These were likely water group cluster ions associated with the plume ionosphere and were found to have masses of up to  $\sim 500$  u/q (Coates et al., 2010). Tenuous atmospheres (exospheres) have been detected around several outer planet moons, primarily produced by the decomposition of surface materials by radiolysis and sputtering due to bombardment from magnetospheric particles. This includes the detection of exospheric O<sub>2</sub> on Europa and Ganymede (Hall et al., 1998) that is thought to be produced mainly by sputtering from energetic heavy ions in the Jovian magnetosphere (Cooper et al., 2001). The environment of the Saturnian inner moons is comparatively depleted in energetic ions due to interactions with neutrals, which are abundant in the inner magnetosphere (Andre et al., 2008; Paranicas et al., 2012, 2018). It is nonetheless expected that sputtering due to bombardment from magnetospheric particles is capable of producing significant exospheres around several of its icy satellites, including Dione and Rhea (Johnson et al., 2008).

At Rhea, the Cassini Ion and Neutral Mass Spectrometer (INMS) detected a weak CO<sub>2</sub>-O<sub>2</sub> exosphere, with column densities roughly  $\sim 2$  orders of magnitude lower than those of the exospheres of Ganymede and Europa (Teolis et al., 2010). Prior to the arrival of the Cassini spacecraft at Saturn, Sittler et al. (2004) predicted that it would be possible to infer exospheres at the planet's icy moons by detecting freshly produced ions that are picked up and accelerated by Saturn's magnetosphere. As illustrated in Figure 1, such freshly produced pickup ions would form a ring distribution with velocity vectors perpendicular to the background



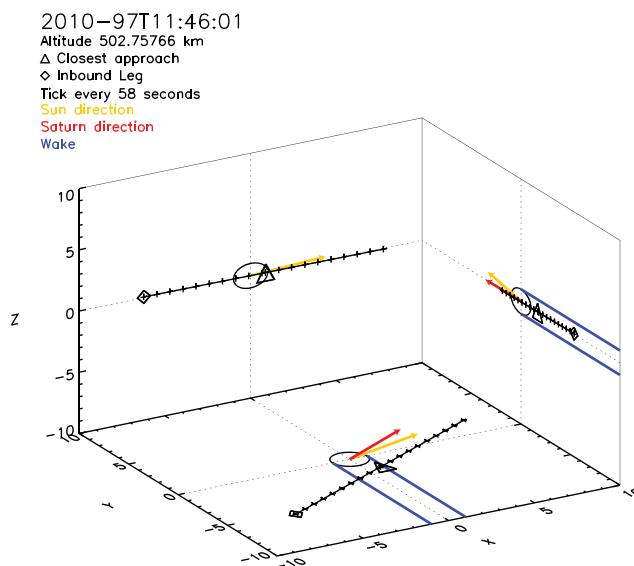
**Figure 1.** Illustration of the ion pickup process at Dione. After Huddleston et al. (1998).

magnetic field and would thus have a distinct pitch angle distribution compared to other magnetospheric particle populations. Indeed, in addition to the neutral particle observations by INMS, CAPS observed  $O_2^+$  and  $CO_2^+$  pickup ions during a close flyby of Rhea (Teolis et al., 2010). During this flyby, CAPS-ELS also observed negative pickup ions that have been suggested to consist of  $O^-$  (Teolis et al., 2010) and heavier carbon-bearing species (Desai et al., 2018). These pickup ions were of likely exospheric origin and were found in ring-like distributions with pitch angles close to  $90^\circ$ .

By studying electron pitch angle distributions, Burch et al. (2007) inferred that a significant source of fresh magnetospheric plasma was located near Dione's orbit. These observations were broadly consistent with the generation of pickup ions at Dione, although the source of these pickup ions was not clear. The Cassini Magnetometer (MAG) (Dougherty et al., 2004) observed magnetic field perturbations consistent with the presence of a significant sputter-induced exosphere (Simon et al., 2011). Subsequently, an oxygen exosphere was inferred from  $O_2^+$  pickup ions observed by the CAPS Ion Mass Spectrometer (CAPS-IMS) instrument (Tokar et al., 2012). The presence of a  $CO_2-O_2$  exosphere was confirmed by observations made by the INMS instrument during subsequent flybys (Teolis & Waite, 2012, 2016). Here we report on the discovery of negative pickup ions during a close flyby of Dione. The observations discussed herein were obtained by CAPS-ELS, which detects the energy per charge ratio of negatively charged particles from 0.6 eV/e to 28.8 keV/e with an energy resolution ( $\Delta E/E$ ) of 16.7%. The instrument consists of eight anodes that are each  $20^\circ \times 5^\circ$  across and oriented in a  $160^\circ$  fan.

## 2. The Dione D2 Flyby

The data discussed herein were acquired during a targeted flyby of Dione that occurred on 7 April 2010 (day of year 97), also referred to as D2. The geometry for this flyby is shown in Figure 2. The Cassini spacecraft passed within 504 km of the moon's surface at a relative speed of 8.4 km/s. The closest approach occurred at 05:16:11 UTC.



**Figure 2.** The trajectory of the Cassini spacecraft during the Dione D2 flyby. The Sun direction (yellow), sub-Saturnian point (red), and nominal plasma wake (blue) are indicated. Units are in Dione radii.

Dione is immersed in magnetospheric plasma which corotates with Saturn's magnetic field. The average corotation flow speed near Dione is ~80% of rigid corotation (Mauk et al., 2009). As the corotation flow speed is significantly greater than the moon's orbital speed, Dione is constantly overtaken by magnetospheric plasma, and a plasma wake can persist for several moon radii downstream of the moon (e.g., Krupp et al., 2013). The D2 flyby occurred downstream of Dione with respect to the corotation plasma flow and the spacecraft passed through the plasma wake near the moon's equator as shown in Figure 2. In the CAPS-ELS data (Figure 3), this can be observed by a dropout in low energy (<10 eV) electrons between ~05:15 and ~05:18 UTC. Additionally, a dropout in electrons above ~300 eV is observed between 05:15:00 and 05:17:30 UTC, indicating the moon's energetic particle shadow. During this time, an additional population of electrons with energies in the 10–30 eV range is observed. These electrons appear to steadily rise in energy as the spacecraft moves further into the wake from the inbound wake flank.

As previously noted by Tokar et al. (2012), the interpretation of observations from the D2 encounter is complicated by the presence of several intense but short-lived enhancements in the hot plasma population (~10 eV to ~10 keV), characteristic of magnetospheric injection events

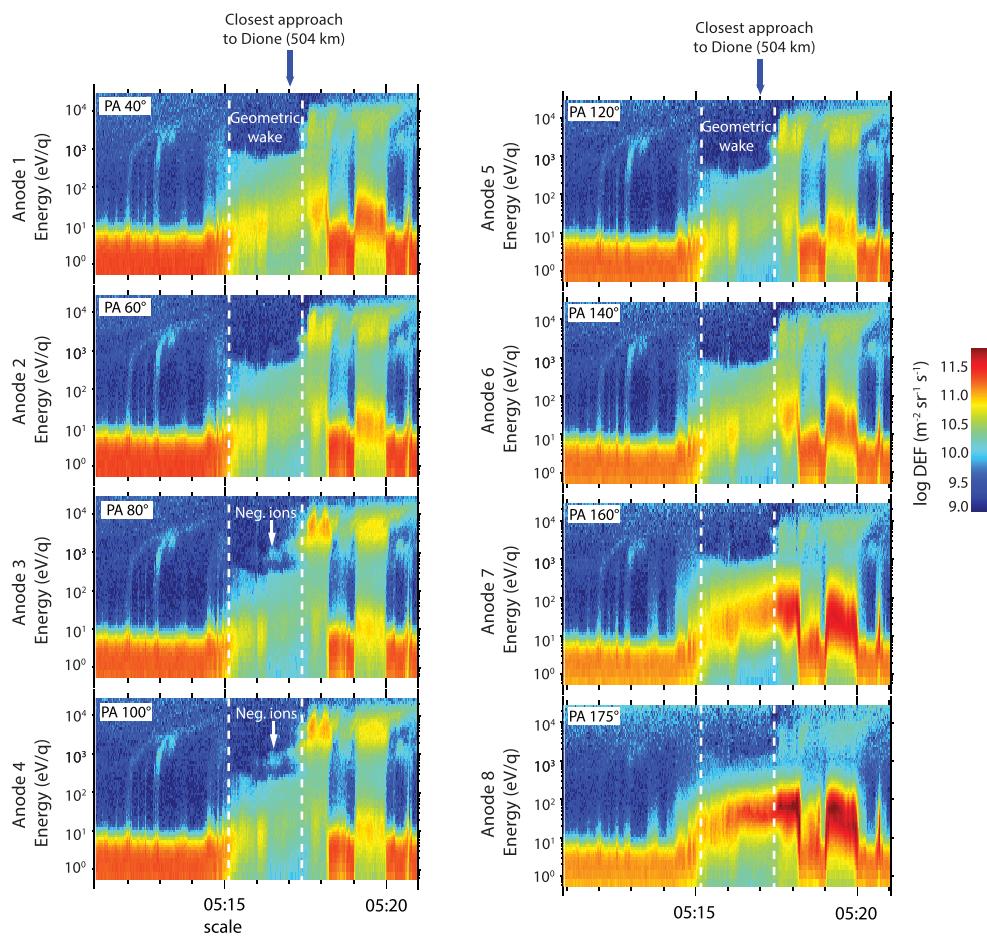
(e.g., Hill et al., 2005; Rymer et al., 2009). Magnetometer observations during the D2 flyby are also consistent with presence of injection events, which are driven by interchange between magnetic flux tubes containing cold and dense plasma, and magnetic flux tubes carrying tenuous and hot plasma (André et al., 2007). The injection events prior to the wake crossing appear to be remote injections as characterized by their energy-time dispersions, while those following the wake crossing appear to be fresh local injections. Near ~05:17 UTC, it appears that the outbound portion of the wake crossing partly overlaps with a local injection, whereas what may possibly be a faint signature of a remote injection can be seen at ~05:16 UTC, approximately halfway through the wake crossing.

In CAPS-ELS Anodes 3 and 4, a relatively long-lived feature near ~600 eV is observed from ~05:15 to ~05:17 UTC. In individual CAPS-ELS spectra (Figure 4), this feature appears as a population between ~400 and ~1,000 eV, with an energy peak located near ~600 eV but rising somewhat in energy over time. During the encounter, CAPS-ELS was oriented such that Anodes 3 and 4 were pointed toward the surface of Dione and the direction of the corotation flow, detecting particles with pitch angles close to 90° (Figure 3). This is consistent with the expected signature of newly produced negatively charged moon-originating pickup ions that have not had time to undergo significant pitch angle scattering and are therefore confined to a ring-like distribution with pitch angles near 90°.

As can be seen in Figure 3, the observed ~600 eV feature is, unlike the remote and local injection signatures, confined to those anodes that have look directions closest to 90° pitch angle, as we would expect for newly produced pickup ions. Nevertheless, the multiple injection events observed throughout this flyby and the fact that the observed ~600 eV feature appears to merge with a local injection at ~05:17 UTC complicate the identification of this feature.

### 3. Analysis

In order to further evaluate the ~600 eV negative particle feature as a possible detection of Dione-originating negative pickup ions, we have carried out tracing calculations for possible pickup ion trajectories. This allows us to determine the possible source region of these particles. First, we define a Cartesian coordinate system at rest with respect to Saturn (the Saturn inertial frame), with the  $x$  axis in the direction of the corotation plasma flow, the  $z$  axis parallel to Saturn's angular velocity, and the positive  $y$  axis in the direction of Saturn. If we consider a source region at rest with respect to Dione, an ion from this source has a velocity in the Saturn inertial frame of  $v_{ion}(t) = v_{ionx}(t)x + v_{iony}(t)y$ . The equations of motion for the ion then become



**Figure 3.** CAPS-ELS spectrograms for Anodes 1–8 during the Cassini flyby of Dione on 7 April 2010. The negative ion candidate feature is indicated by the white arrows. The approximate central pitch angle of each CAPS-ELS anode is shown in the upper left-hand corner of each subplot (pitch angles remained stable throughout the time shown).

$$\begin{aligned} \frac{dv_{ionx}}{dt} + \Omega v_{iony} &= 0 \\ \frac{dv_{iony}}{dt} - \Omega v_{ionx} &= -\Omega V_{flow} \\ \Omega &= \frac{qB}{Mc} \end{aligned}$$

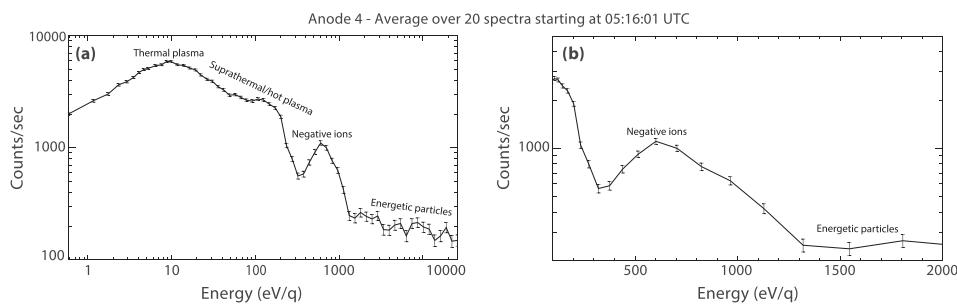
where  $M$  is the mass of the ion,  $\Omega$  is the ion gyrofrequency,  $B$  is the background magnetic field, and  $V_{flow}$  is the velocity of the corotation flow. In the Saturn inertial frame, the expression for the ion velocity becomes

$$v_{ion}(t) = [V_{flow} - (V_{flow} - V_{Dione})\cos(\Omega t)]x - (V_{flow} - V_{Dione})\sin(\Omega t)y.$$

And the trajectory of the ion in the  $x$ - $y$  plane is given by

$$\begin{aligned} x(t) &= x_0 + V_{flow}t - \frac{(V_{flow} - V_{Dione})\sin(\Omega t)}{\Omega}, \\ y(t) &= y_0 + \frac{(V_{flow} - V_{Dione})\cos(\Omega t)}{\Omega} - \frac{(V_{flow} - V_{Dione})}{\Omega}, \end{aligned}$$

with the ion source position located at  $x_0, y_0$  and  $v_{ionx} = V_{Dione}, v_{iony} = 0$  at  $t = 0$ . By considering the look direction  $L$  of the CAPS-ELS anode where the negative ion is detected, we can find the value of  $\Omega t$  when the ion is detected by maximizing the absolute value of the dot product of  $L$  and velocity of the ion in the Cassini



**Figure 4.** Energy spectrum from CAPS-ELS Anode 4 during the D2 flyby (average of 20 spectra starting at 05:16:01 UTC). Shown in (a) is the full CAPS-ELS spectrum with the major particle populations indicated, while (b) shows a close-up around the negative ion candidate feature.

frame,  $v_{ion}(t) - V_{sc}(t)$ , where  $V_{sc}$  is the velocity of the spacecraft in the Saturn inertial frame. With the value of  $\Omega t$  known, we may determine the mass of the ion by considering the observed kinetic energy  $E_{obs}$  of the ion in the Cassini frame

$$M = \frac{2E_{obs}}{(v_{ion} - V_{sc})^2} = \frac{2E_{obs}}{\left[V_{flow} - [V_{flow} - V_{Dione}] \cos[\Omega t] - V_{scx}\right]^2 + \left[-(V_{flow} - V_{Dione}) \sin(\Omega t) - V_{scy}\right]^2}$$

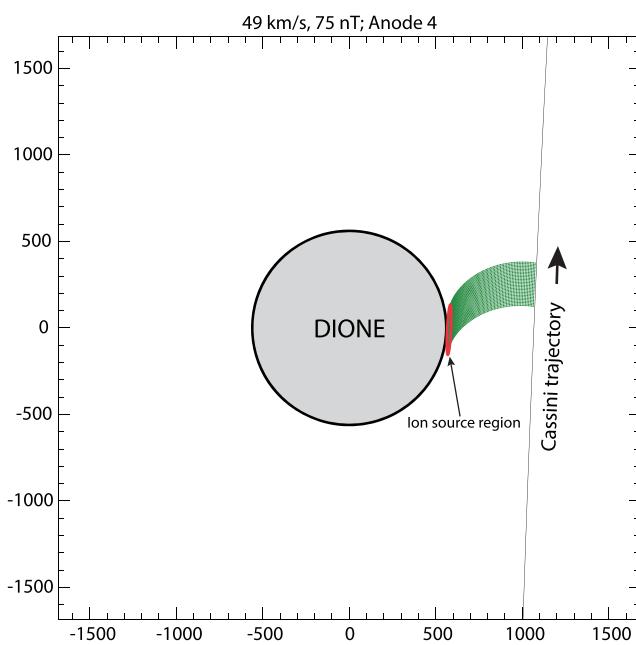
With the value of  $M$  known, we may calculate  $\Omega$ , which in combination with the value of  $\Omega t$  yields the transit time of the ion from the source to Cassini. Using the trajectory equations above, we may then calculate the position of the source region.

Shown in Figure 5 is the predicted source position for the feature seen in CAPS-ELS Anode 4 at  $\sim 600$  eV using a constant value for  $|B|$  of 75 nT (Khurana et al., 2008) and a corotation flow speed of  $49 \pm 6$  km/s for the D2 flyby as given by Tokar et al. (2012). Using these parameters, we find a source region that is located near the surface of Dione. The observed kinetic energy of the particle is consistent with negative ions in the mass range 15–25 u, which we tentatively identify as  $O^-$ . The uncertainty in the negative ion mass estimate is due to the energy resolution of CAPS-ELS as well as the uncertainty in the value of the corotation flow speed at Dione during the D2 encounter.

In order to calculate the along-track negative ion density, we assume that the observed counts multiplied by the ion charge represent a current of ions:

$$n = \frac{C}{A\epsilon v},$$

where  $n$  is the negative ion density,  $C$  is the count rate,  $A = 0.33 \text{ cm}^2$  is the effective area of the instrument estimated from the aperture size and ground calibration data,  $\epsilon$  is the estimated microchannel plate (MCP) efficiency for ions at this bias voltage, and  $v$  is the velocity of the ion into the CAPS-ELS instrument. The CAPS-ELS MCP efficiency for negative ions is not well characterized due to the fact that this instrument was originally designed and calibrated for electrons only (for further details on CAPS-ELS calibration, see Lewis et al., 2008, 2010). Here we use an MCP efficiency for incident  $O^-$  ions of  $\epsilon = 0.4 \pm 0.2$  based on the experimental work of Stephen and Peko (2000). The negative particle feature is observed as an increased count rate in four neighboring energy bins. The central energies of these bins are 514.8, 601.8, 704.3, and 824.0 eV/q. We take an average of the count rate from a 28 s time period (i.e., 14 energy sweeps) starting at 05:16:15 UTC for each of these four



**Figure 5.** The result of particle tracing for the candidate negative ion species using a corotation flow speed of 49 km/s (39 km/s relative to Dione) (Tokar et al., 2012) and a background magnetic field strength of 75 nT (Khurana et al., 2008). Axis units are in km, centered on Dione.

energy bins. In order to subtract the background due to magnetospheric electrons, we use a 6 s average from an earlier time period starting at 05:15:21 UTC. Assuming that the counts in the four energy bins represent negative ions at different gyrophases, we then add these four background subtracted averages together to produce the total count rate  $C$ . If we assume that the negative ions are singly charged, the resulting negative ion along-track density is  $0.0033 \text{ cm}^{-3}$ . We have estimated the upper and lower limits for the negative ion density by considering the uncertainties for the MCP efficiency, instrument effective area, spacecraft potential, background subtraction, and ion energy. The overall uncertainty is dominated by that of the MCP efficiency for negative ions, yielding absolute upper and lower limits for the negative ion number density of  $0.0093$  and  $0.0016 \text{ cm}^{-3}$ , respectively.

#### 4. Discussion and Conclusions

We have reported on a long-lived particle feature that was observed during the D2 flyby of Dione that occurred in 2010 and attributed to possible negative pickup ions. The feature was observed when Cassini passed through Dione's corotation plasma wake, around the time of the spacecraft's closest approach to the moon. By calculating possible particle trajectories, we have determined a source region for these particles that is located near the surface of Dione. While there is some uncertainty in the exact mass of the negative ion species, the calculated mass is consistent with  $\text{O}^-$  ions. Such negative pickup ions were also reported during the Rhea R1 flyby that occurred on 26 November 2005 (day of year 300) (Teolis et al., 2010), and these were originally identified as  $\text{O}^-$ . However, recent work by Desai et al. (2018) has indicated that the feature seen at Rhea may instead be due to a negative ion with a mass of 23–29 u, tentatively identified as  $\text{CN}^-$ ,  $\text{C}_2^-$ , or  $\text{C}_2\text{H}^-$ . These authors also discuss a possible detection of  $\text{O}^-$  pickup ions at a slightly earlier time during this flyby but were unable to make a conclusive identification. In principle, our estimated mass for the Dione D2 negative ion feature could be consistent with the carbon-bearing negative ion species suggested by Desai et al. (2018). However, given the known presence of a  $\text{CO}_2$ – $\text{O}_2$  exosphere and the consistency of our mass estimate with oxygen,  $\text{O}^-$  pickup ions from an exospheric source would appear to be the more likely candidate for the negative pickup ion feature that we observe at Dione.

The observed negative ion feature has an energy peak at  $\sim 600 \text{ eV}$ , yet appears as a broader enhancement over the background magnetospheric electron population that ranges from  $\sim 400$  to  $\sim 1,000 \text{ eV}$ . Due to the large gyro-radii of the pickup ions compared to the source region (e.g., Dione's exospheric scale height is  $\sim 100 \text{ km}$ ), it is unlikely that the velocity ring distribution is completely filled. CAPS therefore would have detected pickup ions at different gyrophases, thus leading to a population that is observed to extend to a broader range of energies. However, we note that it is also possible that this may indicate the presence of several, but less abundant, negative ion species in addition to  $\text{O}^-$ , with energy peaks that are effectively hidden by the limited energy resolution of CAPS-ELS. We note that the negative pickup ions observed at Rhea were also found to have a nongyrotropic distribution (Desai et al., 2018).

It is also worth noting that the negative ion feature was detected and has here been calculated to originate within Dione's corotation plasma wake. During the D2 flyby, Tokar et al. (2012) reported observations of ion acceleration into the wake along the magnetic field. This behavior is predicted for unmagnetized bodies embedded in a plasma flow (Gurevich et al., 1969; Samir et al., 1983) and has been observed at the Earth's moon (Halekas et al., 2014, 2005; Ogilvie & Steinberg, 1996). As ambient plasma moves to fill in the moon's plasma wake, the more mobile electrons will move into the wake ahead of the ions, leading to charge separation and an ambipolar electric field. This electric field leads to acceleration of positive ions into the wake and retards the electrons (Gurevich et al., 1969; Samir et al., 1983). In addition to the accelerated ions reported by Tokar et al. (2012), we note that our observation of a population of hot electrons with steadily rising energy within the wake may also be consistent with the presence of such ambipolar potentials. If such potentials are indeed present in Dione's wake, it is possible that the trajectories of pickup ions may be affected. The infilling of the plasma wake is predicted to occur primarily along magnetic field lines (e.g., Roussos et al., 2008), and thus, any associated charge-separation electric field would be perpendicular to the corotation electric field. This could result in some modification of the pitch angle distribution of pickup ions within the wake region, which may explain why we observe particles with a somewhat larger spread of pitch angles than that expected for an ideal ring distribution.

Based on the CAPS-ELS observations during D2, we have calculated a negative pickup ion density of  $\sim 3 \times 10^{-3} \text{ cm}^{-3}$ . As the count rate remains relatively steady across the time range when the feature is seen, this implies that the O<sup>-</sup> source rate is also relatively constant throughout the source region (e.g., in the vicinity of Dione's surface). The relatively high proportion of negative ions at both Dione and Rhea (as reported by Desai et al., 2018) is somewhat surprising, as cross sections for plausible negative ion formation mechanisms (e.g., dissociative electron attachment to molecular oxygen) are much smaller than the relevant ionization cross sections (e.g., photo and electron impact ionization and charge exchange) for formation of O<sub>2</sub><sup>+</sup> (Itikawa, 2009; Teolis, 2012; Teolis & Waite, 2016). However, it should be noted that these cross sections are given for gas phase interactions. Our tracing results for Dione D2 and those of Teolis et al. (2010) and Desai et al. (2018) for Rhea R1 indicate a negative ion source close to the moon surface. It may therefore be possible that some surface-mediated process, such as dissociative attachment to adsorbed O<sub>2</sub> or CO<sub>2</sub> as suggested by Teolis and Waite (2016), is implicated in the formation of the observed negative ions. Eley-Rideal reactions between incident ions and surface material (Yao & Giapis, 2017a, 2017b) represent another possible negative ion formation pathway that may be relevant to icy moons and that deserves further study. However, we note that the scale height of the Dione exosphere is expected to be quite small, on the order of  $\sim 100 \text{ km}$  (Sittler et al., 2004), and we cannot, given the accuracy of the CAPS observations, distinguish between negative pickup ions originating from the surface itself and those from the exosphere near the surface.

Ionized neutrals are subsequently picked up and accelerated away from Dione, thus representing a potential channel for exospheric loss. Our estimated O<sup>-</sup> density of  $\sim 3 \times 10^{-3} \text{ cm}^{-3}$  is comparable to the O<sub>2</sub><sup>+</sup> pickup ion density of  $1 \times 10^{-2} \text{ cm}^{-3}$  for the D2 flyby estimated by Tokar et al. (2012). This indicates that negative pickup ions may represent a loss channel for Dione's exosphere. In addition, our estimated negative ion density is roughly an order of magnitude higher than that found by Desai et al. (2018) at Rhea, indicating that exospheric loss through negative ion pickup may be a more prevalent at Dione despite the fact that the exospheric densities of the two moons are similar (Teolis & Waite, 2016).

Our findings highlight the importance of negative ion chemistry to our understanding of plasma interactions at icy moons. Negative ions appear to play a role in the interaction of Europa with the Jovian magnetosphere (Desai, Cowee, et al., 2017; Volwerk et al., 2010, 2001), have been found around comets (Burch et al., 2015; Chaizy et al., 1991), and are likely present within the nitrogen-rich ionospheres of Triton, Pluto, and possibly other KBOs (Cheng et al., 2017). These are all high priority targets for upcoming planned and proposed missions, and by observing pickup ions, spacecraft can remotely detect atmospheric or exospheric species at much greater distances than would typically be possible by studying neutral particles with an in situ instrument. The detection of unexpectedly robust populations of negative pickup ions at the Saturnian moons Dione and Rhea highlights the need for a more detailed understanding of negative ion formation and loss mechanisms, including the respective cross sections for these processes at conditions relevant to outer solar system objects.

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