Photodetachment and Test-Particle Simulation Constraints on Negative Ions in Solar System Plasmas

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Abstract

Negative ions have been detected in abundance in recent years by spacecraft across the solar system. These detections were, however, made by instruments not designed for this purpose and, as such, significant uncertainties remain regarding the prevalence of these unexpected plasma components. In this article, the phenomenon of photodetachment is examined and experimentally and theoretically derived cross-sections are used to calculate photodetachment rates for a range of atomic and molecular negative ions subjected to the solar photon spectrum. These rates are applied to negative ions outflowing from Europa, Enceladus, Titan, Dione and Rhea and their trajectories are traced to constrain source production rates and the extent to which negative ions are able to pervade the surrounding space environments. Predictions are also made for further negative ion populations in the outer solar system with Triton used as an illustrative example. This study demonstrates how, at increased heliocentric distances, negative ions can form stable ambient plasma populations and can be exploited by future missions to the outer solar system.

1 Introduction

Negative ions have long been known to exist in astrophysical environments and within the Earth’s ionosphere. They are the major source of opacity within the Sun’s outer layers [Wildt, 1939], appreciate to high densities within interstellar clouds, prestellar cores, and protostellar envelopes [e.g. McCarthy et al., 2006, Cordiner et al., 2013] and can outnumber free electrons in the Earth’s D region [Appleton et al., 1933, Pavlov, 2014]. The Giotto, Galileo, Cassini, Rosetta and Maven spacecraft have found evidence of negative ions existing in abundance within planetary and cometary plasmas with observations at 1P/Halley [Chaizy et al., 1991], Europa [Volwerk et al., 2001], Titan [Coates et al., 2007], Enceladus [Coates et al., 2010a, Teolis et al., 2010], Dione [Nordheim et al., 2020], 67/P Churymov/Gerasimenko [Burch et al., 2015], Mars [Halekas et al., 2015] and Saturn’s ionosphere [Morooka et al., 2019]. These observations were, however, serendipitously made with instruments neither designed nor calibrated for this purpose, and the extent to which negative ions pervade space plasmas is not well constrained. This article describes the phenomenon of photodetachment and examines how this process limits the abundance of negative ions that can exist in solar system collisionless plasmas.

Stable negative ions are produced when an atom or molecule with a positive electron affinity (EA) gains an excess electron. The dominant reactions for producing negative ions in the gas phase include dissociative electron attachment in regions with high fluxes of suprathermal electrons such as at 1P/Halley and Titan [Vuitton et al., 2009, Cordiner and Charnley, 2014], radiative electron attachment reactions in much colder interstellar environments [Herbst, 1981], and electron- and neutral-induced collisional attachment. Negative ions can also be produced from dust grains and solid surfaces via charge inversion due to scattering, secondary emission and sputtering [Wekhof, 1981, Domingue et al., 2014]. The dominant negative ion loss mechanisms include photodetachment, ion-ion recombination, and ion-neutral associative detachment. Proton transfer, polimerisation and charge exchange reactions can also be efficient in producing and destroying negative ions. Crucially, the majority of these processes result from collisional reactions with other ions or neutrals with the exceptions of polar photodissociation and photodetachment.
Polar photodissociation is a relatively minor reaction channel and within the solar system the reaction rates are many orders of magnitude lower than those of photodetachment. For example, the cross section for the production of $\text{H}^-$ from $\text{H}_2$ via this process is of the order of $10^{-23}$ cm$^2$ \cite{Chupka1975}, whereas the photodetachment cross-sections are six orders of magnitude higher, of the order of $10^{-17}$ cm$^2$, see Section 2. Negative ion populations are therefore unable to be sustained within collisionless environments with high photon fluxes.

This theory is consistent with the early identifications of negative ions. Within the Sun’s atmosphere, $\text{H}^-$ is produced within a narrow radial range where the production processes dominate, and indeed do so within all cool stellar photospheres with temperatures less than 7000 K \cite{Wildt1939, Chandrasekhar1943}. Similarly, negative ions have also been observed by sounding rockets and radar observations of the D and lower E region of the Earth’s ionosphere \cite{Johnson1958, Arijs1982}, where collisional reactions enable predominantly halogen- and water-based negative ions to appreciate during the night \cite{Pavlov2014}. In the more distant astrophysical environments the reduced photon flux enables radiative electron attachment to efficiently produce a range of carbon-based negative ions \cite{Dalgarno1973, Herbst1981}.

The recent negative ions detections in the solar system have been made at the interfaces between neutral material and space plasmas. In the inner Coma of 1P/Halley the Giotto spacecraft’s electron spectrometer detected negative ion masses consistent with water- and carbon-based molecules \cite{Chaizy1991} and at 67P/Churyumov-Gerasimenko the Rosetta spacecraft’s electron spectrometer detected negative hydrogen ions produced through the interaction between the solar wind and cometary neutrals \cite{Burch2015}. Similarly, the MAVEN spacecraft detected negative hydrogen ions from the Martian upper atmosphere \cite{Halekas2015}. At Jupiter’s moon Europa, the Galileo spacecraft’s magnetometer observed a negative ion plasma instability which was used to infer the presence of outflowing negative chlorine ions \cite{Volwerk2001, Desai2017}. Within the Saturn system, the Cassini spacecraft’s electron spectrometer detected negative carbon- and/or nitrogen-based ions in Titan’s ionosphere extending up to 13,800 amu/q \cite{Coates2007, 2009, Wellbrock2013, Desai2017, Wellbrock2019, Mihalcescu2020}, which Cassini’s Langmuir Probe found to constitute up to 96\% of the ionospheric negative charge density \cite{Wahlund2009, Agren2012, Shebanits2013, 2016}. Water-based negative ions and dust were similarly detected within the heart of the Enceladus plumes \cite{Coates2010a, Jones2009, Haythornthwaite2020} where they also carried the majority of the negative charge density \cite{Morooka2011}. Further oxygen and possibly carbon-based negative ions populations have also been identified outflowing from Rhea \cite{Teolis2010, Desai2018}, and Dione \cite{Nordheim2020, Tokar2012}. Negative ions and dust have also been shown to dominate in Saturn’s deep ionosphere and, as at Titan and Enceladus, carry the majority of the negative charge and therefore the majority of the planet’s ionospheric plasma mass density due to their large inferred masses \cite{Morooka2019, Shebanits2020}.

This article is laid out as follows; the introduction provides a brief review of negative ions in the solar system and where they have been previously detected. Section 2 then reviews the phenomenon of photodetachment and photodetachment rates are calculated for a number of atomic and molecular negative ion species. Section 3 then uses test-particle simulations to examine how these rates constrain the negative ion detections already made and their subsequent spatial and temporal evolution. Several predictions are also made for further negative ion species likely to be detected. Section 4 then discusses and summarises the key conclusions and makes the case for dedicated negative ion sensors to be carried on future missions to the outer solar system.

## 2 Photodetachment

### 2.1 Theory

Negative ions possess a greater number of electrons than protons, which results in an overall negatively charged atomic ion or molecule. The stability of this negative ion is determined by the EA of the neutral atom \cite{Mulliken1934}. This is a quantitative measure of the amount of energy required to remove an electron from the negative ion. This determines the energy threshold and reaction rates of such a process, and consequently the half-life of a negative ion. The EA can either be a positive or negative
quantity and only atoms or molecules with a positive EA are able to exist in a stable negatively charged state. Approximately 80% of elements in the periodic table have been discovered to possess a positive EA.

Photodetachment is a process where a photon is absorbed by an electron within a negative ion. If the energy of the photon is greater than the electron affinity of the negative ion, the excited electron will have enough energy to be emitted by the atom. In the solar system, the most common source of energetic photons is from the Sun. Figure 1 shows the solar flux of the active and the quite Sun from [Huebner et al., 1992 and references therein], both of which exhibit similar distributions with most of the photons having energies less than ten electron volts, enough to neutralise the majority of negative ions. As a result, electrons that are absorbed by such a photon will have enough energy to be ejected via the reaction sequence,

$$A^- + hv \rightarrow [A^-]^* \rightarrow A + e^-,$$

where $A$ denotes a candidate negative ion, $hv$ denotes a photon, and the $*$ denotes an unstable excited state of the negative ion prior to emitting the excess electron.

### 2.2 Method

In this study, we use the method described by [Huebner et al., 1992] to calculate the photodetachment rates of a range of atomic and molecular negative ions. Ignoring attenuation through mediums, the rate coefficient $k(\lambda_i)$ resulting from the solar flux’s wavelength between $\lambda_i$ and $\lambda_i + \Delta \lambda$ is given by

$$k_i(\lambda_i) = \int_{\lambda_i}^{\lambda_i + \Delta \lambda} \sigma(\lambda) \Phi(\lambda) e^{-\tau(\lambda)} d\lambda,$$

where $\sigma(\lambda)$ is the photodetachment cross section of the negative ion and $\Phi(\lambda)$ is the solar flux at wavelength $\lambda$. However, neither $\sigma$ or $\Phi$ is recorded as a continuous function during observations. If the bin width for $\sigma(\lambda)$ is relatively narrow, the above equation is well approximated by

$$k_i(\lambda_i) = \sigma_i \Phi_i(\lambda_i),$$
Figure 2: Photodetachment cross-sections of (a) H$^-$ and (b) O$^-$ compared to the model of Millar et al. [2007] in Equation 6.

where $\sigma_i$ denotes the average photodetachment cross section between $\lambda_i$ and $\lambda_i + \Delta \lambda$. $\Phi_i(\lambda_i)$ is represented by the given photon flux between $\lambda_i$ and $\lambda_i + \Delta \lambda$ as

$$\Phi_i(\tau_i) = \int_{\lambda_i}^{\lambda_i + \Delta \lambda} \sigma(\lambda)e^{-\tau(\lambda)}d\lambda. \quad (4)$$

The total rate coefficient is thus expressed as

$$k(\tau) = \sum_i k_i(\tau_i). \quad (5)$$

The solar spectrum shown in Figure 1 peaks between 1–10 eV (10$^4$–10$^3$ Å), before decreasing by several orders of magnitude to photon energies near to 10$^4$ eV (∼1 Å). Differences between the quiet and active Sun only become apparent at >10 eV (10$^3$ Å) and therefore do not affect the photodetachment calculations within the accuracy which they can be performed.

The absolute measurement of photodetachment cross-sections of various negative ions is an ongoing research effort [e.g. Lee and Smith, 1979, Best et al., 2011] with drift-tubes, guided ion beams, supersonic beams, and ion traps successfully employed to this end [e.g. Mikosch et al., 2010]. However, much of the emphasis for these experiments has been to calculate the near-threshold behaviour of the photodetachment cross sections, as well as measuring the asymptotic values for larger photon energies. A wide range of experimental data, from near threshold to photon energies of several electron volts, are therefore unavailable for a number of negative ions.

The model described by Millar et al. [2007] provides a prediction for photodetachment cross sections via the relation,

$$\sigma(\epsilon) = \sigma_\infty \sqrt{1 - \frac{EA}{\epsilon}}, \quad (6)$$

where $\sigma_\infty$ is the asymptotic cross section for large photon energies of that ion. This assumes a square-root growth near the threshold, and asymptotic behaviour for photons well above the threshold energy. The near threshold behaviour has been verified by many experiments since then [e.g. Best et al., 2011], however, the asymptotic behaviours well-above threshold do not always match the experimental values. This behaviour is especially significant for smaller ions which have a smaller range of electron binding energies. The photodetachment rates are therefore mostly controlled by the near threshold behaviours, which generally haven’t yet asymptoted to near-constant values. It should also be noted that this model won’t capture strong resonances at photon energies close to threshold which cannot be ruled out in the absence of experimental data Millar et al. [2007].
2.3 Reaction Rates

In this section, photodetachment rates of a range of negative ions at 1 AU are calculated and presented in Table 1. The cross-sections derive from a wide variety of experimental techniques and theoretical calculations, many of which were conducted over 50 years ago. Photodetachment rates, using the model outlined in Equation 6 [Millar et al., 2007], are also compared to and used as the primary method when cross-sectional data is unavailable. To demonstrate the applicability of Equation 6, Figure 2 shows a full range of cross-sections for the negative hydrogen and oxygen ions compared to those predicted by this relationship. The accurate literature derived values, as subsequently described, peak near 2 eV, near $4 \times 10^{-17}$ cm$^2$, before reducing rapidly to less than $5 \times 10^{-18}$ cm$^2$ at larger energies. The model does not capture this early peak instead asymptoting at lower and then higher relative values. On the other hand, larger ions have a broader range of electron binding energies and the cross-sections calculated using Equation 6 better approximate those of the oxygen ion with comparable values up to $\approx 5$ eV where the majority of the solar photon flux lies.

2.3.1 Hydrogen

The $^-$ photodetachment cross-sections are derived from the studies of Geltman [1962], Broad and Reinhardt [1976] and Wishart [1979] which produce values within 1% of each other using J-matrix calculations, quantum perturbation theory, and the close-coupling expansion method with Hylleraas-type correlation terms, respectively. When integrated across the solar spectrum, these cross-sections produce a calculated photodetachment rate of $14.3 \pm 0.143$ s$^{-1}$, which is near the same as that reported by Huebner et al. [1992] using cross-sections of Geltman [1962] and Broad and Reinhardt [1976]. The predicted rate based on Equation 6 is, however, significantly lower at 3.16 s$^{-1}$, calculated using an EA of 0.754 eV Lykke et al. [1991] and assumed asymptotic cross-section of $10^{-17}$ cm$^2$ Millar et al. [2017].

2.3.2 Water-Group

To study water-based negative ion chemistry, we consider the $^-$, OH$^-$ and $[\text{H}_2\text{O}_2]^-\text{O}$ negative ions. Experimentally derived cross-sections for $^-$ for energies up to 4 eV are reported by Branscomb et al. [1965] which agree well with the recent experimental data of Hlavenka et al. [2009]. Above 4 eV, the cross-sections are supplemented with the quantum perturbation theoretical calculations of Robinson and Geltman [1967] although variations at these wavelengths only result in negligible changes to the integrated rate. The photodetachment rate of $^-$ is calculated to be $1.43 \pm 0.07$ s$^{-1}$ and the predicted rate using Equation 6 is $1.51 \pm 0.08$ s$^{-1}$, calculated using an EA of 1.46 eV Chaibi et al. [2010] and asymptotic cross-section of $1.2 \times 10^{-17}$ cm$^2$ Millar et al. [2007].

Experimentally measured cross-sections for both OH$^-$ and $[\text{H}_2\text{O}_2]^-$ are taken from the study of Lee and Smith [1979] and the OH$^-$ cross-sections also agree well with the recent experiments of Hlavenka et al. [2009]. The resultant OH$^-$ photodetachment rate is calculated to be $1.69 \pm 0.0419$ s$^{-1}$ which is similar to $^-$ Equation 6 however predicts a larger photodetachment rate of 2.48 $\pm$ 0.38, calculated using an EA of 1.83 eV Breyer et al. [1981] and asymptotic cross-section of $3.3 \times 10^{-17}$ cm$^2$ Hlavenka et al. [2009]. The photodetachment rates of the larger $[\text{H}_2\text{O}_2]^-$ negative ion are notably lower than these smaller molecules at $0.0688 \pm 0.0172$ s$^{-1}$. Due to the lack of information on a precise EA and reduced cross-sectional measurements, we do not calculate a rate for this molecule using Equation 6.

2.3.3 Halogens

Halogens possess the largest electron affinities in the periodic table and here we consider Cl$^-$, Br$^-$, and F$^-$. Photodetachment cross-sections for these molecules are provided by the quantum perturbation calculations of Robinson and Geltman [1967] which agree well with the experiments of Berry and Reimann [1963]. As the theoretical calculations do not report errors these are estimated from these previous experiments. The Cl$^-$ rate is calculated to be $0.113^{+0.0904}_{-0.0527}$ s$^{-1}$, the Br$^-$ rate $0.235 \pm 0.141$ s$^{-1}$ and the F$^-$ rate $0.0692 \pm 0.0419$ s$^{-1}$. To calculate the associated rates from Equation 6 we take asymptotic cross-sections from Robinson and Geltman [1967] and electron affinities from Berry and Reimann [1963].
The resultant rates fall within the uncertainties of those calculated using the experimentally validated cross-sections.

### 2.3.4 Carbon-based

To represent carbon-based negative ion chemistry, we consider C\(^-\) and the molecular negative ions, CN\(^-\) (where x=1,3,5) and C\(_x\)H\(^-\) (where x=2,4,6). The C\(^-\) cross-sections are taken from Seman and Branscomb [1962] and the resultant photodetachment rate is 4.06 ± 0.29 s\(^{-1}\). The estimated rate from Equation 6 is lower at 3.28 ± 0.29 s\(^{-1}\). The asymptotically measured cross-sections are available for five of the molecular negative ions considered [Best et al., 2011, Kumar et al., 2013], but not C\(_5\)N\(^-\) for which \(\sigma_\infty\) is assumed to be 10\(^{-17}\) cm\(^2\) [Millar et al., 2007]. Due to the lack of experimental data across the full range of energies for these molecules, the Millar et al. [2007] model is used instead. The calculated rates become smaller with increasing mass with the C\(_2\)H\(^-\) rate calculated at 0.0796 ± 0.0199 s\(^{-1}\), the CN\(^-\) rate 0.0399 ± 0.0010 s\(^{-1}\), the C\(_4\)H\(^-\) rate 0.0234 ± 0.00585 s\(^{-1}\), the C\(_3\)N\(^-\) rate 0.0208 ± 0.0106 s\(^{-1}\), the C\(_6\)H\(^-\) rate 0.00799 ± 0.00110 s\(^{-1}\) and the C\(_5\)N\(^-\) rate 0.00248 s\(^{-1}\).

Table 1: Photodetachment rates calculated using estimated and experimental cross-sections for various atomic and molecular negative ions at 1 au. These rates are scaled using an inverse square law to calculate the photodetachment rates used in Section 3.

| Negative Ion Species | Mass [amu] | Electron Affinity [eV] | Asymptotic Cross-section \([10^{-17}\text{cm}^2]\) | Estimated Photodetachment Rate [s\(^{-1}\)] | Accurate Photodetachment Rate [s\(^{-1}\)] |
|---------------------|------------|------------------------|---------------------------------|---------------------------------|---------------------------------|
| H\(^-\)             | 1          | 0.754                  | 1                               | 3.16                       | 14.3 ± 0.1                      |
| C\(^-\)             | 12         | 1.26                   | 2                               | 3.28 ± 0.23                 | 4.06 ± 0.29                     |
| O\(^-\)             | 16         | 1.46                   | 1.2                             | 1.51 ± 0.08                 | 1.43 ± 0.07                     |
| OH\(^-\)            | 17         | 1.83                   | 3.3                             | 2.48 ± 0.38                 | 1.69 ± 0.25                     |
| F\(^-\)             | 18         | 3.40                   | 1                               | 0.0430                      | 0.0692 ± 0.0419                 |
| C\(_2\)H\(^-\)      | 25         | 3.02                   | 0.88                            | 0.0796 ± 0.0199             | –                              |
| CN\(^-\)            | 26         | 3.86                   | 2.84                            | 0.0399 ± 0.0010             | –                              |
| Cl\(^-\)            | 35         | 3.61                   | 4                               | 0.108\(^\pm0.086\)          | 0.113\(^\pm0.090\)              |
| C\(_2\)H\(^-\)      | 49         | 3.56                   | 0.77                            | 0.0234 ± 0.0059             | –                              |
| C\(_3\)N\(^-\)      | 50         | 4.30                   | 5.19                            | 0.0208 ± 0.0106             | –                              |
| [O\(_2\)-H\(_2\)O\(^-\)] | 50 | –                      | –                               | –                           | 0.0688 ± 0.0172                |
| C\(_6\)H\(^-\)      | 73         | 3.80                   | 0.48                            | 0.00799 ± 0.00110           | –                              |
| C\(_5\)N\(^-\)      | 74         | 4.50                   | 1                               | 0.00248                     | –                              |
| Br\(^-\)            | 80         | 3.36                   | 5                               | 0.234 ± 0.141               | 0.235 ± 0.141                   |

[Note. Source code to calculate photodetachment rates as a function of the solar spectrum is available at the Zenodo repository: http://doi.org/10.5281/zenodo.4670382 Zhang et al., 2021, April 7]

# 3 Test-Particle Simulations

## 3.1 Overview

This section uses test-particle tracing simulations to calculate the trajectories of negative ions outflowing from the various bodies where they have been detected. These are combined with the photodetachment rates calculated in Table 1 to constrain their temporal and spatial evolution. The calculations therefore provide a prediction for where they will survive to, and for what fluxes might be detected by future missions or within existing datasets. They also provide context and an estimate of source densities for previous detections already accomplished.

Icy moons constitute the majority of the moons of the outer planets and the detection of subsurface oceans at Europa, Ganymede and Enceladus, has provided key target environments for future missions such as by the ESA JUpiter ICy moon Explorer (JUICE) mission [Grasset et al., 2013] and the NASA Europa Clipper mission [Phillips and Pappalardo 2014]. Icy moons typically possess water-based
surfaces and transient exospheres, both of which provide information on the bulk and trace compositions of the moons themselves and their sub-surface oceans. Figures 3–5 show negatively charged oxygen ions outflowing from Europa, Enceladus, Dione and Rhea, ordered by heliocentric distance, and discussed in order of when the observations were made.

Heavier negative ions have been detected in the inner coma of Comet Halley [Chaizy et al., 1991], in Titan’s ionosphere [Coates et al., 2007] and inferred to be outflowing from Europa [Volwerk et al., 2001]. Table 1 shows that more massive negative ions possess larger electron affinities and are therefore less susceptible to photodetachment processes. To examine heavier negative ions, Figures 6–8 show chlorine outflowing from Europa and CN$^-$ outflowing from Titan as well as Triton which serves to demonstrate negative ions’ increased longevity at increased heliocentric distances.

### 3.2 Method

Newly created negative ions at the interface of space plasma and neutral material will be subjected to the electric field $E = -v \times B$, where $v$ is the bulk plasma velocity and $B$ is the ambient magnetic field. The newly formed negative ion will be accelerated, or ‘picked up’, and gyrate about the magnetic field in accordance with the Lorentz force, and drift in the direction of the bulk plasma flow. The trajectories of newly formed ion populations are calculated in a body-centred cartesian coordinate system where the x-axis points along the direction of plasma flow, the y-axis towards the planet which the body of interest is orbiting, and the z-axis completes the right-handed set. We use the Boris [1970] integration technique to evolve particle trajectories assuming nominal dipolar and interplanetary magnetic fields, and locally measured or predicted plasma velocities. The negative ions are initialised at or up to a given altitude above a target body to represent either surface or atmospheric production. For bodies with a substantial ionosphere which can withstand the incoming plasma flow, the plasma flow upstream is approximated as running perpendicularly to this boundary. Because of these assumptions, ions picked up on an upstream hemisphere are still able to access downstream regions. The electric field therefore results in negative ions being able to escape from a full given hemisphere of a body immersed within a plasma flow.

The photodetachment rates are applied instantaneously at each calculation timestep. The finite number of particles simulated mean that each particle can be thought of as a macroparticle representing a large collection of particles as in the particle-in-cell approximation [Hockney and Eastwood, 1981]. Due to the variation in the measured abundances at the various bodies during different flybys and the instrument uncertainties involved, the particle fluxes are presented as normalised to the maximum density and specific densities and rates discussed alongside in text. The calculated trajectories are therefore generically applicable to existing datasets as well as future observations that might measure different densities and escape rates.

### 3.3 Enceladus

The Cassini spacecraft performed close flybys of Enceladus on multiple occasions and sampled the plumes discovered to be erupting from its south pole [Dougherty et al., 2006]. The electron spectrometer detected negatively charged water group ions [Coates et al., 2010a] and dust grains [Jones et al., 2009] when passing through on flybys E3, E5, E17 and E18 [Hill et al., 2012; Dong et al., 2015] and signatures of which were also seen by the Langmuir Probe [Morooka et al., 2011]. The negative ion masses were identified as distinct peaks in the electron spectrum which were consistent with multiples of 16-18 amu up to 500 amu/q, indicating negative ions derived from water and water-group clusters, such as O$^-$, OH$^-$, and heavier negative water-group ions. The energy resolution of the instrument was optimised for electrons and therefore did not permit more precise mass constraints on these negative ions.

The photodetachment rates of OH$^-$ are similar to that for O$^-$ and, heavier negative water-group ions, approximated here by [O$_2$H$_2$O]$^-$, have photodetachment rates an order of magnitude smaller than these, thus revealing water cluster ions as especially long-lived. The Cassini detections were made deep inside the plume where the plasma had slowed considerably and the negative ions were suggested to be produced from the low speed thermal gas emission and travelling at low velocities of 0.2–2 km/s [Haythornthwaite et al., 2020]. The density of the low mass negative ions of mass range 9–27 amu were observed in the range of 1 – 100 cm$^{-3}$. The densities of negative ions in the constrained range
of 45–70 amu, likely comprising of water cluster ions, were detected at lower densities of \(0.1 – 1 \text{ cm}^{-3}\) \cite{Coates2010}. These densities were however calculated using an instrument detection efficiency of 5\% and subsequent studies \cite{Desai2018, Nordheim2020} use an increased rates of \(\approx 20\%\), derived from the studies of \cite{Peko2000} and \cite{Stephen2000}. The negative ion densities are therefore likely lower than reported by \cite{Coates2010} but with large uncertainties. The uncertainties in the photodetachment rates can therefore be seen to be small compared to uncertainties in the measurements themselves.

The trajectories of these negative ions are calculated assuming a Saturnian dipole field with a field strength at the Enceladus orbit of \(\approx 325 \text{ nT}\) with the particles initialised below the moon’s south pole at various distances from a nominal plume centre with plasma velocities ranging from 1 to 26 km/s. Figure 3 shows a view of the Enceladus south pole with negative oxygen ion trajectories traced and coloured according the their depreciating abundances. At the edge of the plume, assuming a nominal corotational plasma velocity, negative oxygen ions are able to persist for tens of Enceladus radii downstream. If they are picked up in the centre of the plume, however, they are only able to exist within a confined spatial extent of a few tens of kilometres. \([\text{O}_2\text{-H}_2\text{O}]^-\) would however survive for significantly longer than this as the distance travelled downstream can be scaled by the photodetachment rate. The Cassini detections were possible due to the spacecraft ram velocity which boosted the energy in the spacecraft frame such that they could be detected by the electrostatic analyser. The trajectories and lifetimes depicted in Figure 3b therefore confirms that, due to their relatively short lifetimes, these negative ions were produced deep within the Enceladus plume.

Ion cyclotron waves have been observed throughout the Enceladus Neutral Cloud and E-ring \cite{Meeks2016} with amplitudes peaking near Enceladus and inferring large quantities of pickup ions \cite{Cowee2009}. The intense radiation fluxes near-saturate the plasma detectors \cite{Taylor2018} which makes direct pickup ion identification difficult. Ion cyclotron waves therefore present an alternative method for detecting negative pickup ions, as at Europa \cite{Volwerk2001}, as the wave polarisation will be left-handed for positive ions and right-handed for negative ions \cite{Desai2017}.

### 3.4 Rhea

The detection of negative ions by the Cassini spacecraft at Rhea contributed to the discovery of the moon’s sputter-induced oxygen and carbon dioxide exosphere \cite{Teolis2010}. These negative ions were initially identified as \(\text{O}^-\) \cite{Teolis2010} but their energies, and therefore masses, were later identified as consistent with heavier carbon-based negative ions such as \(\text{CN}^-, \text{C}_2\text{H}^-, \text{C}_2\) or \(\text{HCO}^-\) \cite{Desai2018}. Rhea and other icy moons possess unidentified dark patches at near-infrared wavelengths.
which has been highlighted as evidence for carbonaceous compounds [Scipioni et al., 2014] from which carbon-based negative ions might originate [Johnson, 1993]. Several processes could however increase oxygen pickup ion energies to this increased energy and, given how little is known about this distant environment, it remains an open question as to which negative ions were detected. The negative fluxes were observed up to densities over $5 \times 10^{-3}$ cm$^{-3}$ [Desai et al., 2018]. The uncertainty on this can be reasonably assumed as 17 % corresponding to the energy resolution of the instrument, which is therefore of a similar magnitude to the error in the O$^-$ photodetachment rate, but smaller than the error in the CN$^-$ photodetachment rate, see Table 1.

The trajectories of outflowing O$^-$ and CN$^-$ are calculated assuming a Saturnian dipolar magnetic field of $\approx 26$ nT at Rhea’s orbit and a plasma velocity of 60 km/s [Wilson et al., 2010]. Figure 4 and 4 shows the resultant trajectories and depreciating abundances for negative ions initialised at Rhea’s surface, with illumination and plasma conditions representative of the R1 encounter where they were detected. These show that the oxygen ions would depreciate to 1 % of their source densities within 10 Rhea radii and by nearly a quarter by the time they had reached Cassini. An oxygen composition therefore corresponds to source production rates $\approx 25$ % higher than those reported of over $6.25 \times 10^{-3}$ cm$^{-3}$. Carbon-based negative ions would however survive significantly longer, with CN$^-$ surviving up to over 500 Rhea radii downstream before depreciating by the same levels. Carbon-based negative ions would therefore be considered to have suffered negligible losses en-route to Cassini from the moon.

3.5 Dione

Dione was discovered to possess a sputtered-induced oxygen and carbon dioxide exosphere [Tokar et al., 2012]. During D2, the second flyby of Dione, the Cassini spacecraft detected fluxes of outflowing negative ions within the moon’s wake consistent with negative ions of masses 15–25 amu/q [Nordheim et al., 2020]. These were therefore identified as O$^-$ with densities of $\approx 3 \times 10^{-3}$ cm$^{-3}$, comparable to those of the positive ion outflows [Tokar et al., 2012].

These negative ion detections were made just 1000 km downstream of the moon and therefore within the particles first gyration around the magnetic field. The particle trajectories shown in Figure 5 assume a Saturnian dipole field of $\approx 75$ nT at Dione’s orbit with particles spawned on Dione’s surface where the detections have been identified as originating [Nordheim et al., 2020]. The particle trajectories show that
negative oxygen ion fluxes will survive to nearly 15 Dione radii downstream before decreasing to 1 % of their source values. The normalised abundances also show that by the time of the detections during the second Cassini-Dione conjunction D2, photodetachment losses would have been a noticeable loss channel and that the sources fluxes would be approximately 25% higher than those reaching the Cassini spacecraft, nearer $4 \times 10^{-3}$ cm$^{-3}$. As at Rhea, the uncertainties in these densities can be considered to derive from the 17 % energy resolution of the instrument, which is of a similar magnitude to the errors in the photodetachment rate.

3.6 Europa

3.6.1 Water-Group

Europa possesses an oxygen exosphere [Hall et al., 1995] and large sub-surface water ocean [Khurana et al., 1998]. Hubble observations have also provided tentative plume detections [Roth et al., 2014, Sparks et al., 2016] and the Galileo spacecraft observations have been shown to be consistent with their presence [Jia et al., 2018, Huybrighs et al., 2020]. Negative oxygen ions are therefore likely to be produced in a similar fashion to at Enceladus within the putative plumes via electron attachment reactions, or sputtered from the water-ice surface as at Dione, and possibly Rhea, via surface mediated processes resulting from the intense Jovian radiation environment [Van Allen et al., 1975]. The trajectories of outflowing negative oxygen ions are calculated in Figure 6 assuming a dipolar magnetic field strength at Europa of $\approx 400$ nT with particles initialised only in the visible x-z plane, 100 km above the Europan surface. The trajectories reveal that negative oxygen ions can survive to approximately 4 Europa radii downstream before depreciating by two orders of magnitude. This distance might be lower if the plasma velocity is slowed significantly near the moon, as was sometimes observed [Kivelson et al., 2009]. Figure 3a shows that the presence of negative oxygen ions, or further water group negative ions which would survive for even longer, could be important in interpreting bulk plasma current measurements from Langmuir Probe or Faraday Cup instruments in this region, depending on their source densities.

3.6.2 Chlorine

Europa’s surface is predominantly water-ice but contains dark streaks within cracks in the icy shell which Hand and Carlson [2015] find are consistent with heavily irradiated chlorine compounds originating from the moon’s ocean. Outflowing positive and negative chlorine ions were inferred to exist by the polarisation of ion cyclotron waves [Volwerk et al., 2001] observed by the Galileo spacecraft in the moon’s plasma wake. Hybrid simulations by Desai et al., 2017b support this hypothesis and use the wave amplitudes to calculate source densities in the range of $0.1 - 1$ cm$^{-3}$.

The trajectories of Cl$^-$ are calculated as outlined in Section 3.6. Figure 6 shows these and reveals that fluxes are able to survive up to $\approx 50$ Europan radii downstream before decreasing to 1 % of their source.
Figure 6: Cl$^-$ outflowing from Europa. The trajectories are coloured according to the normalised maximum density. $R_{\text{Europa}} = 1561$ km.

densities. This is significantly further downstream then where Galileo observed right-handed wave power at the chlorine ion gyrofrequency at just 3-4 Europan radii [Volwerk et al., 2001]. The photodetachment rates therefore indicate that local fluxes in this region would be representative of the source production, whether globally or locally produced. It is also interesting to note the $\text{C}_2\text{H}_x^-$ negative ions are also predicated as a potential sputter product at Europa [Johnson, 1993].

Figure 7: (a) CN$^-$ outflowing from Titan. The trajectories are coloured according to the normalised maximum density. $R_{\text{Titan}} = 2576$ km.

3.7 Titan

Titan’s ionosphere contains an abundance of carbon- and nitrogen-based ion and neutral chemistry, including, negative ions with masses up to 13,800 amu/q [Coates et al., 2007, 2009]. Within the broad mass spectrum distinct peaks were identified at 25.8–26.0 and 49.0-50.1 amu/q belonging to the carbon chain anions CN$^-$/C$_3$N$^-$ and/or C$_2$H$^-$/C$_4$H$^-$. [Desai et al., 2018], which extend right up to near Titan’s exobase near 1400 km. Chemical models predict these carbon chain anions [Vuitton et al., 2009] and also
the lighter negative hydrogen ion $\text{H}^-$ [Mukundan and Bhardwaj, 2018] although this is below the lower end of the mass detection threshold of Cassini’s spectrometer and so was not detected.

Global hybrid simulations of Titan’s plasma interaction [Ledvina and Brecht, 2012] were found to be highly dependent on the negative ions within Titan’s ionosphere. These simulations predict large quantities of 20-70 amu negative ions escaping from the ionosphere and being picked up and drifting downstream. In Figure 7, the trajectories of these negative ions are calculated assuming Saturnian dipolar magnetic fields of $\approx 6$ nT at Titan’s orbit and a bulk plasma velocity of 100 km/s, with particles initialised only at the equatorial regions of Titan to visually highlight the large gyroradius relative to the moon. Figure 7 shows negative ions fluxes are able to survive for extended distances and reach $\approx 300$ Titan radii downstream before depreciating to 1% of their source densities.

Larger carbon-based negative ions are also predicted to escape and will survive for even greater distances due to their lower photodetachment rates, see Table II. While such negative pickup ions haven’t been detected as yet, positive pickup ions have been [Regoli et al., 2016] and Figure 7 therefore provides a prediction for where outflowing negative ion fluxes would persist to.

3.8 Triton

Triton possesses a nitrogen and methane hazy atmosphere [Broadfoot et al., 1989] with highly electronegative molecules like at Titan. Photochemical processes have been observed as instigating Titan’s negative ion chemistry through the production of suprathermal electron populations which produce Titan’s low-mass negative ions [Mihai1escu et al., 2020]. Despite the reduced solar photon flux at Triton’s $\approx 30$ au heliocentric distance, the Voyager 2 spacecraft observed a large ionosphere which was explained by the influx of magnetospheric plasma [Hoogeveen, 1994] with sufficient energies to produce negative ions such as CN$^-$ [Vuitton et al., 2009, Mihai1escu et al., 2020].

The Neptunian dipole is highly inclined and rotating and the dynamics of trapped particles populations are surely a research end in itself. The trajectories of outflowing CN$^-$ are calculated within a magnetospheric configuration of a dipole field inclined 45° relative to Triton’s orbital plane, with a Neptunian dipole moment of $2.2 \times 10^{17}$ Tm$^{-3}$. Figure 8 shows the traced abundances of the candidate CN$^-$ negative ion and shows that negative ions such as CN$^-$ would form a full torus of negative ions over 24 hours in magnetic local time before the fluxes depreciate to 1% of their source densities.

The low photodetachment rates at these heliocentric distances reveal negative ions as capable of forming stable magnetospheric populations which can be used to probe the composition of the Neptunian and Uranian moons, as well as transport processes within these complex magnetospheric configurations.

Figure 8: CN$^-$ outflowing from Triton. The trajectories are coloured according to the normalised maximum density. $R_{\text{Neptune}} = 24622$ km. Neptune is to scale but Triton is magnified to make visible.
4 Discussion & Conclusions

This study was motivated by the spate of negative ion detections in solar system plasmas over the past thirty years. The method of [Huebner et al., 1992] was used to calculate the photodetachment rates of a range of atomic and molecular negative ions subjected to the solar photon spectrum, as presented in Table 1. Significant effort was made in deriving as complete and accurate set of cross-sectional data as possible, much of which was derived from experimental studies conducted over fifty years ago. The results of these calculations were compared to photodetachment rates calculated using the theoretical relationship of [Millar et al., 2007]. This approach proved accurate for larger molecules, as long as an accurate electron affinity and asymptotic cross-section at larger photon energies had been determined. For the smaller molecules examined, H\(^-\), C\(^-\), O\(^-\), and OH\(^-\), this method, however, proved to be inaccurate. The newly calculated photodetachment rates spanned four orders of magnitude with decreasing photodetachment rates corresponding to increasing mass, a trend which can be attributed to the increased electron affinity of the larger molecules negating regions of the solar spectrum where the photon flux is highest.

The photodetachment rates were then scaled by heliocentric distance and test-particle simulations used to constrain the nominal escape trajectories of negative ion populations at various bodies in the outer solar system. Negative water-group ions are constrained at Europa and Enceladus, negative oxygen ions at Rhea and Dione, negative chlorine ions at Europa, and negative carbon-based ions at Titan and Rhea. These detections were made with instruments not specifically designed for detecting negative ions and significant uncertainties therefore exist on the reported densities. For this reason, the escaping fluxes were normalised to the source densities thus leaving the results as broadly applicable to existing as well as future measurements.

The photodetachment rates of negative ions derived from water-based negative ion chemistry provided several interesting insights. O\(^-\), OH\(^-\), and negative water cluster ions such as \([\text{O}_2\text{-H}_2\text{O}]^-\), were identified as presenting a viable detection aim at the Jovian icy moons, with heavier negative cluster ions being particularly resistant to photodetachment processes. These rates also had interesting implications in the Saturn system. At Dione, the detected negative ions were shown to have already undergone significant photodetachment losses and the source negative oxygen ion production rates are therefore inferred to be \(\approx 25\%\) greater than those measured in-situ [Nordheim et al., 2020]. This would also be true for O\(^-\) populations detected at Rhea although ambiguities remain as to whether the detected negative ions consisted of O\(^-\) or heavier carbon-based species [Desai et al., 2018] which would have undergone negligible photodetachment losses. It was also found that the stagnated plasma flow in the Enceladus plume mean that locally detected water group ions are confined to a limited spatial domain.

Heavier negative ions possess increased electron affinities and the corresponding photodetachment rates provided several further interesting insights. At Europa, negative chlorine ion densities were found to persist for up to 50 Europa radii downstream and sufficiently long to power the wave activity at the chlorine gyrofrequency observed by Galileo [Volwerk et al., 2001; Desai et al., 2017], but not long enough to contribute to the Europen plasma torus [Bagenal et al., 2015]. At Titan, CN\(^-\) escaping from the moon’s extended ionosphere could survive for \(\approx 300\) Titan radii downstream and are thus predicted to form an extended negative ion tail. They are therefore also able to constitute a significant part of the moon’s plasma interaction as predicted by [Ledvina and Brecht, 2012].

In addition to these aforementioned locations, negatively charged hydrogen has been detected at 67P/Churyumov-Gerasimenko and at Mars, produced via double charge exchange with the solar wind [Burch et al., 2015; Halekas et al., 2015], and likely do at many, if not all, unmagnetised, bodies interacting directly with the solar wind. The persistence of such fluxes will be strongly controlled by photodetachment which will evolve as such during their highly elliptical orbits.

The negative ion populations considered have all been found to exist within collisionless solar system plasmas surrounding moons, comets and Mars. The equatorial ionosphere of Saturn has, however, also been found to contain large populations of negatively charged ions and dust which comprise up to over 95 % of the negative charge density [Morooka et al., 2019]. These have significant consequences for the ionospheric dynamics [Shebanits et al., 2020] and the spacecraft-plasma interaction experienced by Cassini [Zhang et al., 2021]. Saturn’s polar wind has been observed as a significant mass source for its magnetosphere [Felici et al., 2016] and if negatively charged ions and aerosols exist within the polar...
regions, these will also mass load the magnetosphere with negative ion populations. While these will be relatively short lived outside of Saturn’s shadow, polar winds at Uranus and Neptune might produce long-lived ambient magnetospheric populations of negative ions.

Of further mention is that negative ions will persist within collisionless plasmas if not exposed to direct sunlight. The trajectories presented in Figures 3 and 4 are calculated for predominantly sunlit conditions and it should therefore be noted that for specific body-planet geometries negative ions might persist for significantly longer. At 9 am planetary magnetic local time an orbiting body’s plasma wake will be completely in shadow and negative ions escaping downtail will therefore survive until reaching sunlight. Similarly, if negative ions are produced within the shadow of a planet they will survive for extended periods where losses can only result from infrequent collisions with ions and neutrals, extraplanetary photon fluxes or transport into other regions.

While most negative ions have only recently been detected within the solar system, it is worth mentioning that their presence was predicted at bodies with tenuous atmospheres over 40 years ago. Wekhof [1981] considered negative ions could be formed at Mercury, the Moon and Europa, via sputtering and charge inversion processes, and constitute a few percent of the negative charge density. Further bodies subjected to similar sputtering processes, such as asteroids, further moons and Mercury [Domingue et al., 2014], therefore also present environments where negative ions might persist.

The photodetachment rates are considerably reduced at increased heliocentric distances due to the reduced solar photon fluxes. To illustrate this concept, CN$^-$ fluxes were modelled escaping from Triton’s large ionosphere, and were found to survive for 24 hours of magnetic local time thus forming a negative ion torus around Neptune. Future missions to the outer solar system are therefore well-placed to use such populations as a diagnostic tool using dedicated instrumentation [e.g. Lepri et al., 2017], whose presence may be necessary to wholly and accurately describe the surrounding environments.

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