PHOTOCHEMISTRY OF PLANETARY IONOSPHERES

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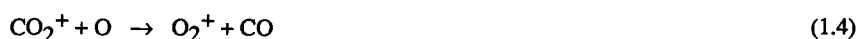
ABSTRACT

The basic photochemical processes in the upper atmospheres and ionospheres of the various bodies in our solar system (planets, moons and comets) are similar. However, there are many different factors (e.g. gas composition, energy input, gravity) which control/change the relative importance of these controlling processes. The photo-chemistry of the inner planets is reasonably well understood at this time, thus there is good agreement between model calculations and most of the observational data base. The extremely limited information that we have available on the ionospheres of the outer planets leads to significant uncertainties about some of the controlling processes. Some important questions (e.g. Is the charge exchange process $H^+ + H_2(v \geq 4) \rightarrow H_2^+ + H$ important? Is water vapor influx from the rings important?) remain unanswered at this time. In cometary atmospheres the freshly evaporated parent molecules are rapidly photodissociated and photoionized, therefore most of the chemical kinetics of cometary ionospheres involve these rapidly moving and highly reactive ions and radicals.

INTRODUCTION

In this paper, because of space limitations, only the ionospheres of Venus, Saturn and comet P/Halley are discussed. Each of these ionospheres are significantly different, yet they all clearly demonstrate the important role that chemistry plays in establishing their structure and composition.

VENUS

It has been known for decades that the dominant constituent of Venus' atmosphere is CO_2, therefore early models of its ionosphere were based on pure CO_2 assumptions (e.g./1/). These early, basically photochemical models, published shortly after the flyby of Venus by Mariner 5 /2/, were relatively successful in reproducing the measured electron density profiles. The next major advance in our understanding of the ionosphere of Venus occured in 1974, just before the Mariner 10 radio occultation data became available /3/, with the publication of the work by Kumar and Hunten /4/ . These authors showed that an atomic oxygen mixing ratio, even as low as 1% near the homopause, has a major impact on the photochemistry, resulting in molecular oxygen being the major ion near the ionization peak. In other words, it was predicted that the most abundant ion is O_2^+ even though there is practically no molecular oxygen in the Venus atmosphere. This prediction of Kumar and Hunten /4/ and those of other similar later models /5, 6/ were borne out by the ion mass spectrometer measurements of the Pioneer Venus Orbiter /7/.
The dominant photochemical reactions, based on our present understanding of the Venus ionosphere, are:

$$CO_2 + h\nu \rightarrow CO_2^+ + e \tag{1.1}$$

$$\rightarrow CO^+ + O + e \tag{1.2}$$

$$\rightarrow CO + O^+ + e \tag{1.3}$$

$$CO_2^+ + O \rightarrow O_2^+ + CO \tag{1.4}$$

$$O^+ + CO_2 \rightarrow O_2^+ + CO \tag{1.5}$$

$$O_2^+ + e \rightarrow O + O \tag{1.6}$$

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A more detailed block diagram of the ion chemistry is shown in Figure 1 and a comprehensive table of ion-neutral reactions of possible interest for the ionosphere of Venus is reproduced here (Table I) from Nagy et al. /8/; further reactions of possible importance, including ones involving metastable species, can be found in Fox /9/. Photochemical models based on these reactions have been very successful in reproducing the overall daytime electron density and major ion variations in the photochemically controlled region, below about 200-km. Figure 2 shows the observed solar zenith angle dependence of the peak electron density, along with some calculated values /10/. Figure 3 shows the measured and calculated diurnal variations of O_2^+ and O^+ at 200-km /11/, which is close to the transition altitude from chemical to diffusive control. The agreement between the observed and calculated values of O^+ and O_2^+ is good, indicating a reasonable understanding of the major ion photochemistry, while the significant disagreements shown for CO_2^+ and NO^+ demonstrate that we still have a way to go for a detailed knowledge of all the processes controlling the minor ion chemistry on Venus. Fox /9/ has demonstrated that metastable species play an important role in the chemistry of some of the minor ions and was able to eliminate some of the discrepencies between the measured and calculated values (see for example, the comparison for N^+ shown in Figure 4).
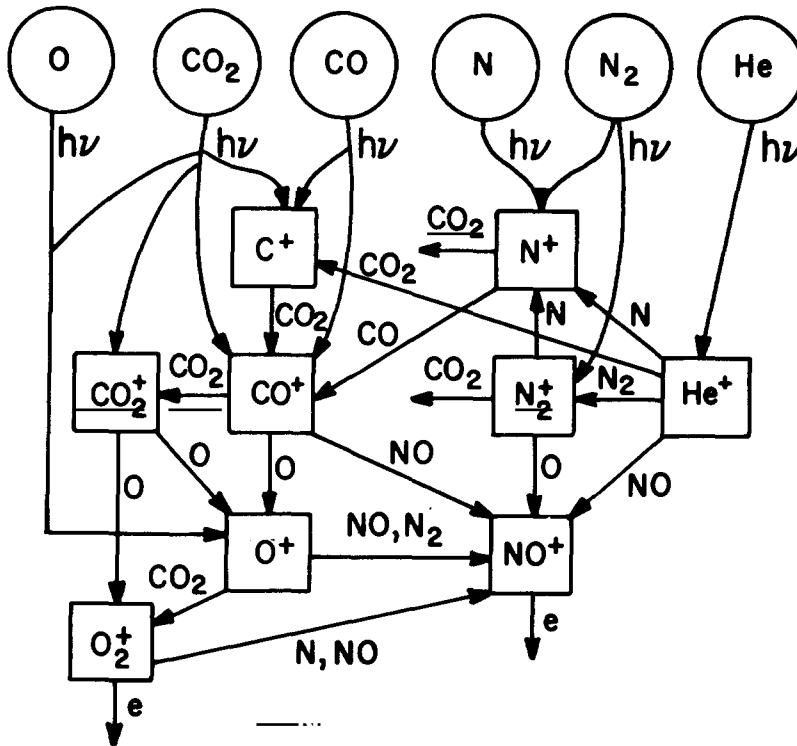

Fig. 1. Block diagram of the major ion chemistry scheme in the Venus ionosphere (from /8/).

SATURN

The flybys of Saturn, by Pioneers 10 and 11 and Voyagers 1 and 2, provided us with a number of electron density profiles of its ionosphere. Numerous models of Saturn's ionosphere were generated before and after these encounters, however all these models have had some problems matching the observations with the calculated values (cf. /12/).

The major neutral constituent in Saturn's upper atmosphere is H_2, therefore the major primary ion which is formed by either photoionization or particle impact is H_2^+. Particle impact ionization results in similar products as does photoionization, therefore, for the sake of brevity it is not included in the following general discussion. Photodissociation and ionization of the main neutral constituent, H_2, in the upper atmosphere leads to:
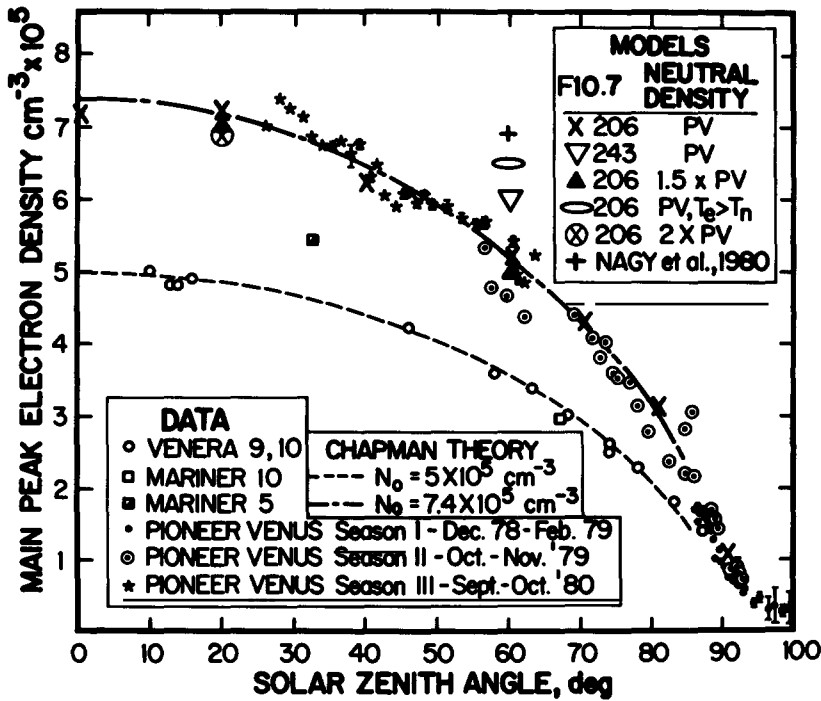
Fig. 2. Electron number densities at the ionospheric peak versus solar zenith angle (from /11/).
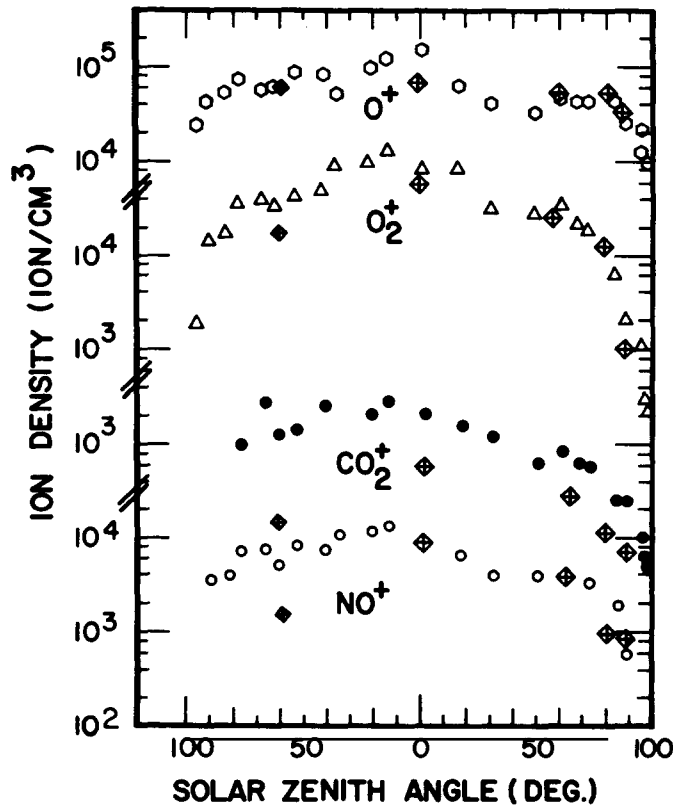

Fig. 3. Measured and calculated (represented by diamonds) daytime ion density variations of O^+, O_2^+, CO_2^+ and NO^+ at 200 km (from /33/).
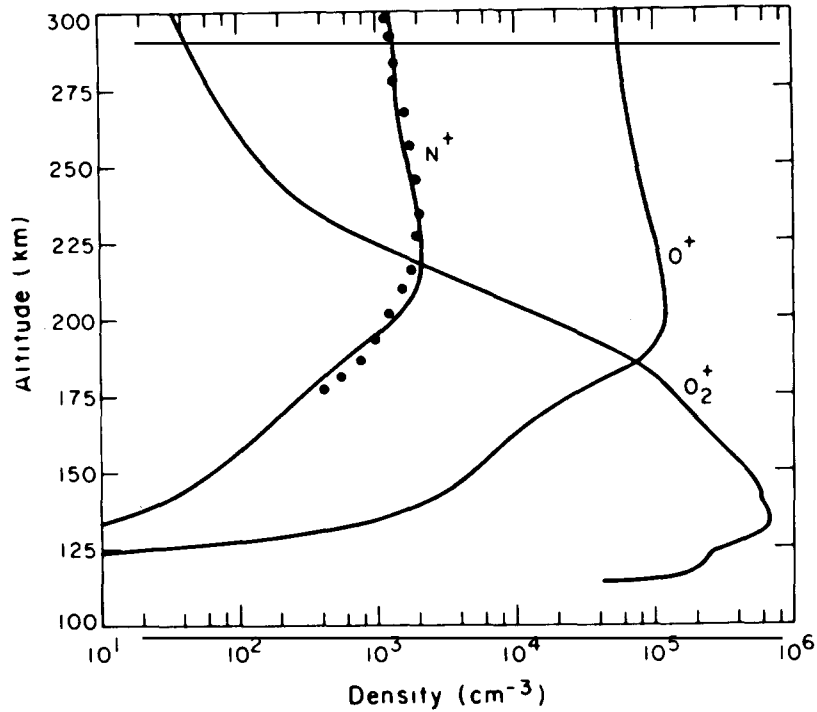
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Fig. 4. Measured (solid circles) and calculated (solid lines) N^+ densities for Venus (from /9/).

$$H_2 + h\nu \rightarrow H + H \tag{2.1}$$

$$\rightarrow H_2^+ + e \tag{2.2}$$

$$\rightarrow H + H^+ + e \tag{2.3}$$

The neutral atomic hydrogen can also be ionized:

$$H + h\nu \rightarrow H^+ + e \tag{2.4}$$

Radiative recombination, which is extremely slow ($\sim 10^{-12}$ cm^{-3} s^{-1}), is the only direct recombination mechanism available for H^+. H_2^+ is very rapidly transformed to H_3^+, which then undergoes dissociative recombination:

$$H_2^+ + H_2 \rightarrow H_3^+ + H \tag{2.5}$$

$$H_3^+ + e \rightarrow H_2 + H \tag{2.6}$$
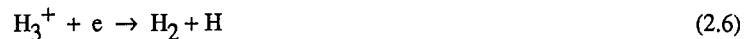
The dissociative recombination rate was believed to be very rapid /13/, but recent measurements indicate that it is a very slow process unless H_3^+ is in a vibrationally excited state with v>3 /14, 15/. This is not necessarily a problem because reaction (2.5) generally results in a vibrationally excited H_3^+; however this issue needs further attention.

Models based upon the above discussed chemical processes, predict an ionosphere which is predominantly H^+, because of its long lifetime ($\sim 10^6$ s). In these models H^+ is removed by downward diffusion to the vicinity of the homopause (~ 1100-km), where it undergoes charge exchange with heavier gases, mostly hydrocarbons such as methane, followed by dissociative recombination. An example of such a model electron density profile is that reproduced in Figure 5 (cf. /12/); the measured Voyager 2 electron densities (cf. /12/) are also shown in this Figure for comparison. The main difficulties with these model ionospheres, with "hydrogen only" upper atmospheres, are that:

1) the ionospheric density at the apparent main peak is about an order of magnitude larger than the observed one;
2) the altitude of the calculated ionospheric main peak is much lower than the observed one; and
3) the predicted long lifetime of H^+ is inconsistent with the observed major diurnal variations (see Figure 6) in the electron density peak /16/.
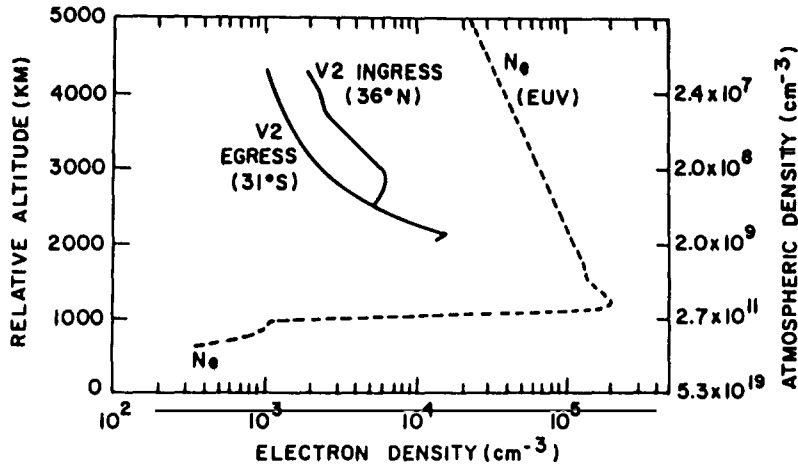

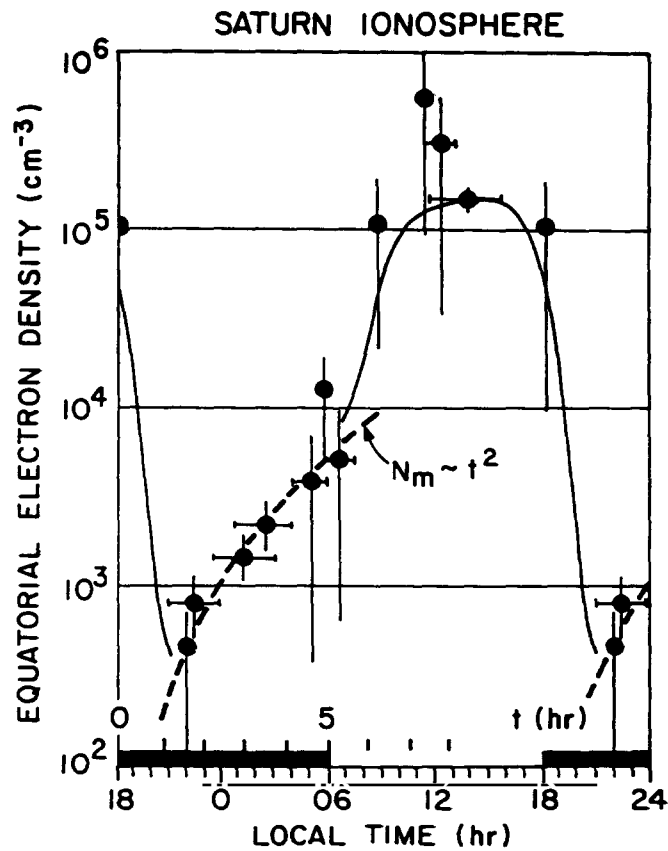Fig. 5. Measured and calculated electron density profiles for Saturn (cf. /12/).

Fig. 6. Measured equatorial electron concentrations as a function of local time at Saturn (from /16/)

To overcome some of these difficulties a number of suggestions have been put forward during the last few years. Kliore et al. /17/ mentioned the possible effects of ionospheric drifts and ring shadowing. Atreya and Waite /18/, following an earlier suggestion by McElroy /19/, examined the possible role of vibrationally excited H_2, in reducing the calculated value of the electron density. Molecular hydrogen in a vibrationally excited state greater than 4, has sufficient energy for the following charge transfer processes:

$$H^+ + H_2(v{\geq}4) \rightarrow H_2^+ + H \tag{2-7}$$

Transforming some of the H^+ to H_2^+ increases the effective loss rate and thus reduces the predicted electron densities. There have been some quantitative calculations of the vibrational energy distribution of H_2 in Jupiter's upper atmosphere and the related electron density reductions /20/. No such calculations have been published for Saturn; however unpublished work by Cravens (personal communication) indicates that reasonably elevated vibrational temperatures cannot account for the major discrepencies between the calculated and observed electron densities for Saturn.

The most recent models of the Saturn ionosphere by Connerney and Waite /21/, Majeed and McConnell /22/ and Waite and Cravens /23/ are based on the earlier suggestions of Shimizu /24/, Ip /25/ and Chen /26/, that water from the rings is being transported into Saturn's upper atmosphere and modifies the photochemistry of the ionosphere. The presence of H_2O results in H^+ being transformed first into H_2O^+ and then H_3O^+, through a catalytic process involving H_2O, as indicated in Figure 7 (some of the more important reactions are given in Table II). The resulting rapid loss of H^+ and the recent indications of a slower recombination rate for H_3^+, result in a steady state model ionosphere dominated by H_3^+ (e.g. /23/). In reality such steady state conditions will not prevail, and it is expected that H_3O^+ and H^+ dominate during the day, with H_3^+ becoming important at night. Simple calculations by Connerney and Waite /21/ and more recent and comprehensive calculations by Majeed and McConnell /22/ and Waite and Cravens /23/ have shown that a downward flux of water from the rings into the atmosphere, in the range of 1-$10{\times}10^7$ cm^{-2} s^{-1} does lead to electron densities consistent with the observations (see Figure 8). The next step which needs to be taken to advance our understanding of Saturn's ionosphere is the development of time dependent models; such efforts are in progress with some results ready to be published in the near future.
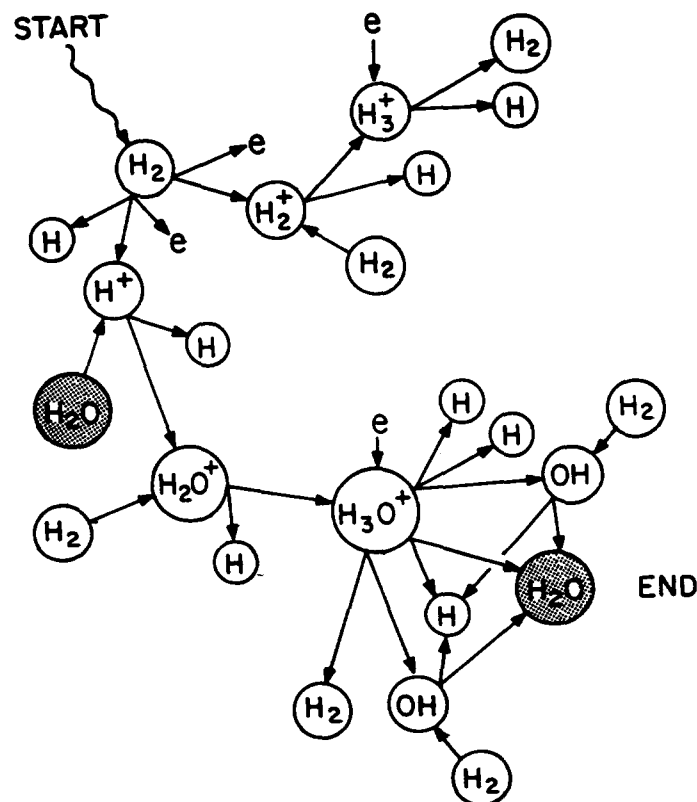
SATURN IONOSPHERE
(WATER MODEL)

Fig. 7. Block diagram of the chemistry scheme, involving water, for the ionosphere of Saturn (from /23/).
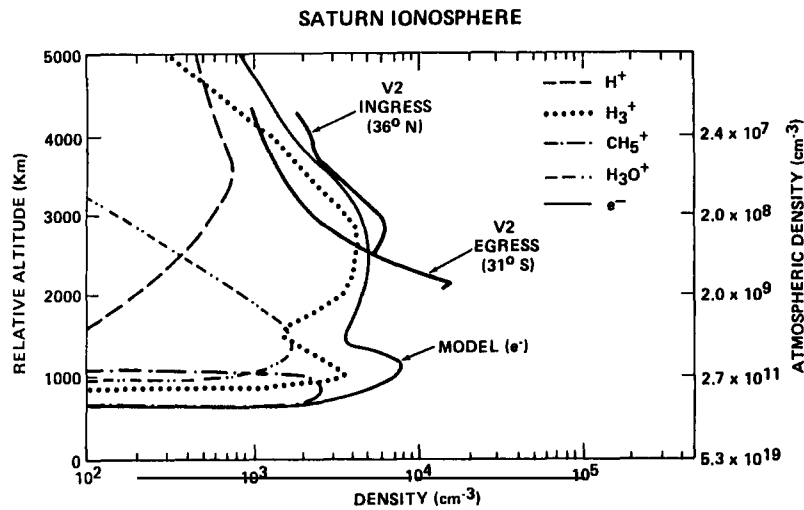
Fig. 8. Calculated and measured (solid lines) ion densities for the ionosphere of Saturn. The calculations take into account the influx of water and a soft electron precipitation source (from /23/).

COMET HALLEY

The atmospheres of comets, commonly referred to as comas, are different in a number of important ways from planetary atmospheres. The most important distinguishing characteristics of comas are (1) the lack of any significant gravitational force, (2) relatively fast radial outflow velocities, and (3) the time-dependent nature of their physical properties. A direct consequence of these features is the expanding nature of cometary atmospheres. The neutral mass spectrometer instrument carried by the Giotto spacecraft /27/, which came within ~600-km of the nucleus, established that water was the main gaseous constituent throughout the encounter. More specifically, it established that water vapour accounts for more than 80% of the gases escaping the comet. Krankowsky et al. /27/ also found that the CO_2, NH_3 and CH_4 mixing ratios are 3.5%, 10% and 7% respectively (the last two values are upper limits). This experiment also obtained an estimate of 900 ± 200 m s^{-1} for the neutral gas expansion velocity, which agrees well with the values predicted by past model calculations (cf /28/).

The predominance of water vapor in the atmosphere of comet Halley has led to a number of first order, "water" models of the ionosphere (cf. /29/). The main photochemical processes involved in such a model are:

$$H_2O + h\nu \rightarrow H_2O^+ + e \tag{3.1}$$

$$\rightarrow H^+ + OH + e \tag{3.2}$$

$$\rightarrow OH^+ + H + e \tag{3.3}$$

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH \tag{3.4}$$

$$H_2O^+ + e \rightarrow OH + H \tag{3.5}$$

$$\rightarrow O + H_2 \tag{3.6}$$

$$H_3O^+ + e \rightarrow OH + H_2 \tag{3.7}$$

$$\rightarrow OH + H + H \tag{3.8}$$

$$\rightarrow H_2O + H \tag{3.9}$$

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The large rate coefficient for reaction (3.4) means that the major ion in a water dominated atmosphere of comets, such as Halley, is H_3O^+; Figure 9 shows the calculated dominant ions from a model of Mendis et al. /29/. The characteristic transport time is comparable to the chemical recombination time throughout the ionosphere of a comet such as Halley. It was shown by Korosmezey et al. /30/ that the electron density varies roughly as $1/r$, where r is the radial distance from the nucleus, uder both photochemical and transport controlled conditions, if the transport velocity is constant.
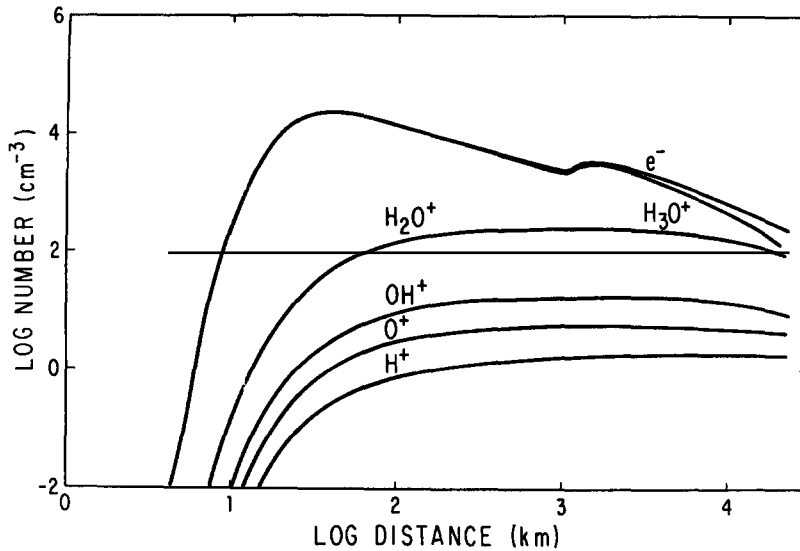

Fig. 9. Calculated radial profiles of the electron and major ion densities for conditions corresponding comet Halley at 0.89 AU (from /29/).

The Giotto spacecraft carried two mass spectrometers which were capable of measuring the ion composition in Halley's ionosphere /27,31/. The neutral mass spectrometer, operating in the ion mode /27/ found that the H_3O^+/H_2O^+ ratio increases with decreasing distance from the nucleus and exceeds unity at distances <20,000-km.

Detailed variations of the ions measured by the ion mass spectrometer /31/ are shown in Figure 10. These preliminary results show that the simple photochemical models were successful in predicting the nature of the major constituents in comet Halley's ionosphere, but it is also clear that in order to understand the details of the chemistry and other properties (e.g. energetics and dynamics) of the ionosphere much more comprehensive models need to be developed (e.g. /32, 30/).
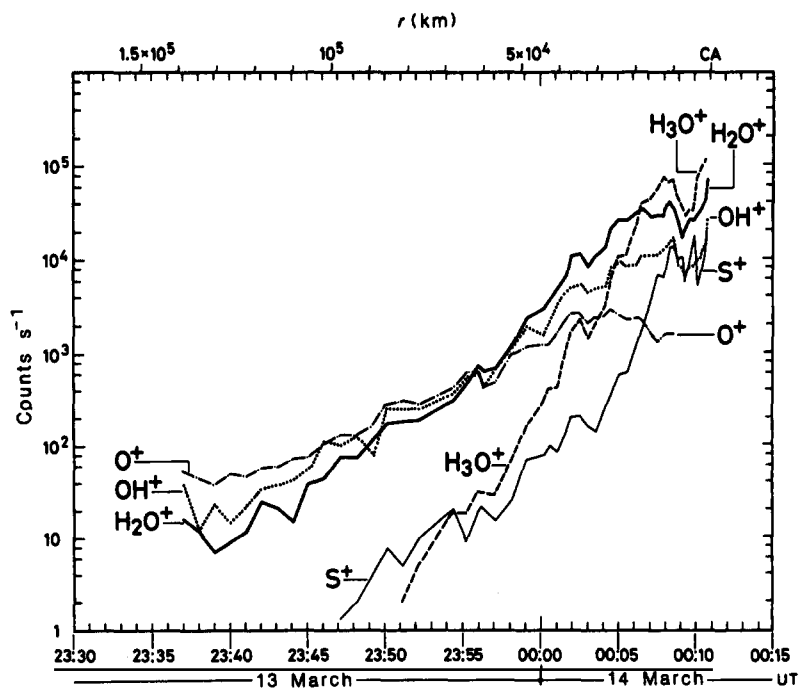

Fig. 10. The measured variations of the major ions along the Giotto trajectory (from /31/).

SUMMARY

As stated in the introduction the three ionospheres selected for discussion were intended to demonstrate the importance of photochemistry in establishing the nature of a given ionosphere. The chemistry, energetics and dynamics of the atmospheres of these three planets are widely different and therefore the resulting ionospheres are also significantly different. The best explored planetary ionosphere, besides the terrestrial one, is that of Venus, therefore it is one which we understand most. The very recent in situ exploration of comet Halley elucidated some of the unknown ionospheric parameters, and although much remains to be studied, we do have some very basic information now available to advance our understanding of its ionosphere. The ionosphere of Saturn is the one we know the least about and no significant advances are expected until new observations can be carried out (e.g. Cassini mission).

ACKNOWLEDGEMENTS

TABLE I
Ion-Neutral Reaction Rates[a]

Reaction Number	Reaction	Rate Constant $(cm^3 s^{-1})$
N1	$CO_2^+ + O \rightarrow O^+ + CO_2$	9.6×10^{-11}
N2	$CO_2^+ + O \rightarrow O_2^+ + CO$	1.64×10^{-10}
N3	$CO_2^+ + NO \rightarrow NO^+ + CO_2$	1.2×10^{-10}
N4	$CO_2^+ + H_2 \rightarrow CHO_2^+ + H$	1.4×10^{-9}
N5	$CO_2^+ + H \rightarrow CHO^+ + O$	5.0×10^{-10}
N6	$CO_2^+ + H \rightarrow H^+ + CO_2$	1.0×10^{-10}
N7	$CO_2^+ + N \rightarrow products$	$\leqslant 1.0 \times 10^{-11}$
N8	$CO^+ + O \rightarrow O^+ + CO$	1.4×10^{-10}
N9	$CO^+ + CO_2 \rightarrow CO_2^+ + CO$	1.0×10^{-9}
N10	$CO^+ + NO \rightarrow NO^+ + CO$	3.3×10^{-10}
N11	$CO^+ + H_2 \rightarrow COH^+ + H$	1.8×10^{-9}
N12	$CO^+ + N \rightarrow NO^+ + C$	$\leqslant 2.0 \times 10^{-11}$
N13	$O_2^+ + NO \rightarrow NO^+ + O_2$	4.5×10^{-10}
N14	$O_2^+ + N \rightarrow NO^+ + O$	1.2×10^{-10}
N15	$N_2^+ + CO \rightarrow CO^+ + N_2$	7.4×10^{-11}
N16	$N_2^+ + CO_2 \rightarrow CO_2^+ + N_2$	7.7×10^{-10}
N17	$N_2^+ + NO \rightarrow NO^+ + N_2$	3.3×10^{-10}
N18	$N_2^+ + O \rightarrow NO^+ + N$	1.4×10^{-10} [b]
N19	$N_2^+ + O \rightarrow O^+ + N_2$	1×10^{-11} [c]
N20	$C^+ + CO_2 \rightarrow CO^+ + CO$	1.1×10^{-9}
N21	$O^+ + N_2 \rightarrow NO^+ + O$	1.2×10^{-12}
N22	$O^+ + NO \rightarrow NO^+ + O$	6.4×10^{-13}
N23	$O^+ + CO_2 \rightarrow O_2^+ + CO$	9.4×10^{-10}
N24	$O^+ + H_2 \rightarrow HO^+ + H$	1.7×10^{-9}
N25	$O^+ + H \rightarrow H^+ + O$	$2.5 \times 10^{-11} T_n^{1/2}$
N26	$N^+ + CO \rightarrow CO^+ + N$	4.0×10^{-10}
N27	$N^+ + CO \rightarrow NO^+ + C$	5.0×10^{-11}
N28	$N^+ + NO \rightarrow NO^+ + N$	9.0×10^{-10}
N29	$N^+ + CO_2 \rightarrow CO^+ + NO$	2.5×10^{-10}
N30	$N^+ + CO_2 \rightarrow CO_2^+ + N$	7.5×10^{-10}
N31	$He^+ + CO_2 \rightarrow CO^+ + O + He$	8.7×10^{-10}
N32	$He^+ + CO_2 \rightarrow CO_2^+ + He$	1.2×10^{-10}
N33	$He^+ + CO_2 \rightarrow O^+ + CO + He$	1.0×10^{-10}
N34	$He^+ + CO \rightarrow products$	1.68×10^{-9}
N35	$He^+ + CO \rightarrow C^+ + He + O$	1.4×10^{-9}
N36	$He^+ + NO \rightarrow N^+ + He + O$	1.25×10^{-9}
N37	$He^+ + N_2 \rightarrow N^+ + He + N$	9.6×10^{-10}
N38	$He^+ + N_2 \rightarrow N_2^+ + He$	6.4×10^{-10}
N39	$H^+ + CO_2 \rightarrow CHO^+ + O$	3.0×10^{-9}
N40	$H^+ + O \rightarrow O^+ + H$	$2.2 \times 10^{-11} T_n^{1/2}$
N41	$H^+ + NO \rightarrow NO^+ + H$	1.9×10^{-9}

[a] Data are taken from Albritton (1978), D. G. Torr and M. R. Torr (1978), and Schunk and Raitt (1980).
[b] $300/T^{0.44}$ for $T \leqslant 1500$ K.
[c] $300/T^{0.23}$ for $T \leqslant 1500$ K.

Table II

Photochemical Reactions of Possible Importance for the Ionospheres of Saturn and Comets*

	Rate**
$H_2O + h\nu \rightarrow OH + H$	1.0×10^{-5} s^{-1}
$\rightarrow OH^+ + H + e$	5.5×10^{-8}
$\rightarrow H_2 + O(^1D)$	1.4×10^{-6}
$\rightarrow H_2O^+ + e$	3.3×10^{-7}
$\rightarrow H_2 + O^+ + e$	5.8×10^{-9}
$\rightarrow H^+ + OH + e$	1.3×10^{-8}
$H + h\nu \rightarrow H^+ + e$	7.3×10^{-8}
$H_2 + h\nu \rightarrow H + H$	4.5×10^{-8}
$\rightarrow H_2^+ + e$	5.4×10^{-8}
$\rightarrow H + H^+ + e$	9.5×10^{-9}
$OH + h\nu \rightarrow O + H$	1.8×10^{-5}
$H_2^+ + H_2 \rightarrow H_3^+ (\nu \geq 3) + H$	2×10^{-9} $cm^{-3}s^{-1}$
$H_2^+ + H \rightarrow H^+ + H_2$	6.4×10^{-9}
$H_3^+ + H_2 \rightarrow H_3^+ + H_2$	3×10^{-10}
$H^+ + H_2O \rightarrow H_2O + H$	8.2×10^{-9}
$H^+ + H_2 (\nu \geq 4) \rightarrow H_2^+ + H$	$\sim 2 \times 10^{-9}$ ***
$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$	2.05×10^{-9}
$H_2O^+ + H_2 \rightarrow H_3O^+ + H$	6.1×10^{-10}
$H^+ + e \rightarrow H + h\nu$	2×10^{-12}
$H_2^+ + e \rightarrow H + H$	$< 10^{-8}$
$H_3^+ + e \rightarrow H_2 + H$	***
$\rightarrow H + H + H$	***
$H_3O^+ + e \rightarrow H_2O + H$	$2.33 \times 10^{-7}(T/300)^{-0.5}$
$\rightarrow OH + H_2$	$2.33 \times 10^{-7}(T/300)^{-0.5}$
$\rightarrow OH + H + H$	$2.33 \times 10^{-7}(T/300)^{-0.5}$
$H_2O^+ + e \rightarrow OH + H$	$5.32 \times 10^{-7}(T/300)^{-0.5}$
$\rightarrow O + H_2$	$1.5 \times 10^{-7}(T/300)^{-0.5}$

*Taken from Atreya et al. (1984), Connerney and Waite (1984), and Mendis et al. (1985)

**Photoionization frequencies are normalized to 1 AU

*** See text for discussion and references

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