

# A Two-Dimensional Model of Ion Composition in the Stratosphere

## 1. Positive Ions

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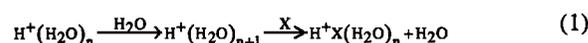
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Ion composition measurements have shown that the dominant ions are mainly proton hydrates (PH) (or  $H^+(H_2O)_n$ ) in the upper stratosphere and mesosphere and nonproton hydrates (NPH) (or  $H^+ X (H_2O)_m$ ) in the lower stratosphere. Theoretical and experimental studies have indicated that the identity of X is almost certainly methyl cyanide ( $CH_3CN$ ). This paper reports a two-dimensional model of ion composition from 15 km to the stratopause. The model accounts for the latitudinal variation in the ionization rate by galactic cosmic rays and in the concentration of neutral species which affect ion chemistry. The results obtained indicate several new and interesting features. The altitude of the crossover point of PH over NPH is found to vary with latitude. The PH ions start to dominate as low as 27 km near the poles, whereas at the equatorial latitude, NPH ions remain the dominant ions up to about 45 km. The modeled profiles at 45°N, the only latitude at which experimental data are available, conform very well to those data. The ion composition is found to be highly dependent on the reaction rate coefficient (K) for the conversion of NPH to PH, which is poorly known. The meridional distribution of ion composition and a comparison with the available observational data is presented. Finally, the need for future ion composition measurements at other latitudes is emphasized.

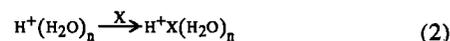
### 1. INTRODUCTION

At ionospheric levels, ion chemistry is reasonably well understood. However, below the stratopause, there is a much greater variety of neutral reactive species that participate in ion chemistry and the chemistry becomes correspondingly more complex. In recent years, considerable progress has been made toward achieving better understanding of ionic processes occurring in this region. During the past decade, several in situ ion composition measurements have been reported [Arijs *et al.*, 1978, 1983, 1984; Arnold *et al.*, 1978; Ingels *et al.*, 1986]. All these measurements were made from middle-latitude stations (44°N). No attempt has been made so far to measure the stratospheric ion composition at other latitudes. The dominant ions observed at mid-latitude above about 38 km have been attributed to the type  $H^+(H_2O)_n$  called proton hydrates (PH), whereas below this altitude, ions of the type  $H^+ X (H_2O)_m$  called nonproton hydrates (NPH) were found to dominate. Neutral trace species have been shown to play a major role in the formation of PH and NPH ions. Initially, the identity of X, which is responsible for the conversion of PH to NPH, was not known. It is now widely accepted that the formation of NPH results from the reaction of PH with methyl cyanide ( $CH_3CN$ ) (also called acetonitrile). Several model studies of ion composition in the middle atmosphere were carried out after the first ion composition measurements were made [Thomas, 1983; Brasseur and Chatel, 1983; Arijs and

Brasseur, 1986; Beig and Chakrabarty, 1987, 1988]. For the theoretical model study, mainly two approaches are possible. One is to use an ion scheme which contains all the chemical processes taking place at that altitude. The ion first produced in this region is  $O_2^+$  which finally terminates to PH and NPH after undergoing various reactions. Details of these reaction channels and their rates are not yet properly known. For example, it is not known whether  $H^+ X (H_2O)_n$  is formed by water clustering of PH and then by switching reaction

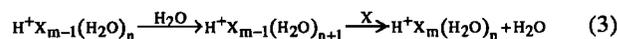


or by direct acetonitrile clustering reaction

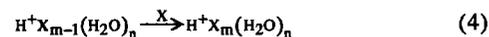


or by both processes.

Similarly, it is not clear if the multiple of X takes place through



or directly through



No laboratory information about these processes is available for (2) and (4). Nevertheless, detailed models of stratospheric ion composition were made by some authors [e.g., Brasseur and Chatel, 1983; Thomas, 1983] who

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considered only processes (1) and (3). Later, *Arijs and Brasseur* [1986] considered all the channels (1), (2), (3), and (4) but ignored the back reaction channels (reverse reactions) for the process (1). However, these model studies were based on a limited knowledge and several assumptions. An alternative approach is to use a simplified scheme in which all the known channels are considered and to substitute all the intermediate reaction channels by a single channel whose reaction rate is carefully chosen. In the past, such an attempt was made by *Beig and Chakrabarty* [1988]. In the present paper we have also taken the simplified approach to minimize the number of assumptions and the complexity of the model.

Although the lifetime of stratospheric ions is quite short, the ion composition is nevertheless indirectly controlled by dynamical processes. For example, the latitudinal variation of long-lived species such as  $\text{H}_2\text{O}$  and particularly  $\text{CH}_3\text{CN}$ , should be reflected in the positive ion composition. Some of the parameters which are directly connected with the ion chemistry are also expected to vary with latitude. This is the case in particular for the ionization by cosmic rays. However, in the past, due to the lack of experimental data on ion composition (other than those gathered at mid-latitudes) and due to the poorly understood chemistry of neutral species, mainly  $\text{CH}_3\text{CN}$ , no meridional models of ion composition were proposed.

The above considerations have shown that it is necessary to extend the previous one-dimensional model studies of the lower middle atmosphere to two-dimensional studies. In this paper we report a two-dimensional ion composition model for the altitude range of 15 to 55 km. In this model study, the meridional fields of the neutral species density, the temperature distribution, and the required transport parameters have been calculated with a more refined two-dimensional model and are used as input data in the simplified ion chemical scheme to construct the model of ion composition.

## 2. TWO-DIMENSIONAL MODEL AND NEUTRAL SPECIES

The model used to simulate the behavior of neutral species in the atmosphere is an updated version of the two-dimensional model described by *Brasseur et al.* [1990]. It extends from the surface to the mesopause and from the south to the north pole with a spatial resolution of  $5^\circ$  in latitude and 1 km in altitude. Chemical, radiative, and dynamical processes are treated interactively above 15 km altitude, while below this level, the dynamical parameters (wind, eddy diffusivity, temperature) are specified.

In the stratosphere and mesosphere the transport equations are expressed in the transformed Eulerian mean framework [*Andrews and McIntyre*, 1976; *Boyd*, 1976]. Momentum deposition and eddy diffusivities are expressed as a function of the mean dynamical state of the atmosphere through the parameterization of *Lindzen* [1981] and *Holton* [1982] for the contribution of gravity wave breaking and through the formulation of *Hitchman and Brasseur* [1988] for the contribution of Rossby wave absorption. Solar heating as well as photodissociation rates of molecules are calculated by integrating over up to 171 wavelength intervals of the solar irradiance absorbed in the atmosphere. Multiple scattering is treated according to the method of *F. Luther* (private communication, 1978). Infrared cooling is derived from the radiative code used in the National Center for Atmospheric Research (NCAR) community climate model (CCM1); see *Kiehl*

*et al.* [1987]. The chemical scheme includes about 60 species belonging to the oxygen, nitrogen, hydrogen, chlorine, bromine, fluorine, carbon, and sulfur families. Because the system of chemical equations is mathematically stiff, due to the large dispersion in the chemical time constants of the several species, a "family grouping" technique is used to solve these equations [see *Brasseur et al.*, 1990]. Relatively large time steps can therefore be used to integrate the model. No diurnal variations are explicitly considered, but seasonal effects in solar and dynamical forcing are taken into account.

Examples of calculated distributions of trace gases affecting the chemistry of positive ions in the middle atmosphere are shown in Figures 1 and 2. The mixing ratio of water vapor above the tropopause, shown in Figure 1, is characterized by a region of low values (approximately 2 parts per million by volume (ppmv)) in the tropics near 15–20 km. This is in accord with the Brewer-Dobson theory that dry air is injected by the Hadley cell and transported toward higher latitudes. Consistently with the global observations provided, for example, by the limb infrared monitor of the stratosphere (LIMS) instrument on board the *Nimbus 7* satellite [*Remsberg et al.*, 1984], the calculated water vapor mixing ratio increases as a function of altitude as a result of methane oxidation and reaches approximately 5 ppmv near the stratopause. The model, however, does not reproduce the high concentrations (5–7 ppmv) observed by LIMS near the tropopause at high latitudes, which are believed to be due to the injection of  $\text{H}_2\text{O}$  from below through a mechanism that is not yet understood and therefore not accounted for in the model. This problem does not significantly affect the calculated values of the total PH and NPH densities.

The meridional distribution of methyl cyanide is shown in Figure 2a. This atmospheric constituent is released in the atmosphere as a result of combustion processes (including biomass burning and the use of internal combustion engines) and direct emission from industrial waste. The molecule is destroyed by the OH radical in the atmosphere [*Arijs and Brasseur*, 1986] and perhaps taken up by oceans [*Hamm and Warneck*, 1990]. The mixing ratio decreases from about 10 pptv at 20 km to less than 1 pptv at the stratopause. This vertical gradient is weaker in the tropics than at higher latitudes, due to the circulation patterns which produce upward transport near the equator and downward transport in the polar regions. A vertical profile calculated by the model at mid-latitudes ( $45^\circ\text{N}$ ) is compared in Figure 2b with a number of direct and indirect determinations of the  $\text{CH}_3\text{CN}$  concentration, including measurements at the surface by *Snider and Dawson* [1984] and near the tropopause by *Arnold and Hauck* [1985]. The shape of this profile is consistent with observations, although the model appears to slightly overestimate the mixing ratios between 20 and 30 km altitude. The difference could be explained by the existence of an unidentified destruction mechanism in the lower stratosphere, an inappropriate choice in the surface boundary condition (fixed mixing ratio of 20 pptv) or inaccuracies in the measurements.

## 3. ION CHEMICAL SCHEME

The ion chemical scheme used in this study has been described elsewhere in detail [*Beig and Chakrabarty*, 1987, 1988] and is shown in Figure 3. The major source of ionization below the stratopause is galactic cosmic rays. The associated ion pair formation rate has been calculated by the

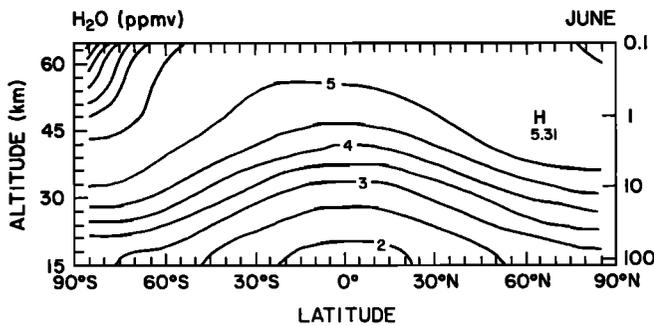


Fig. 1. Meridional distribution of water vapor mixing ratio (parts per million by volume) (ppmv) derived by the two-dimensional model. June conditions. Contour intervals: 0.5 ppmv.

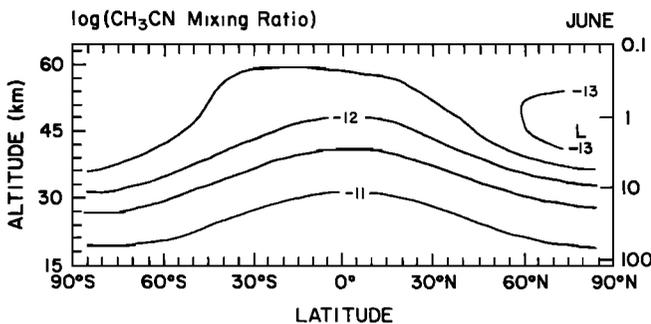


Fig. 2a. Meridional distribution of methyl cyanide mixing ratio (logarithmic scale) derived by the two-dimensional model. June conditions. Contour intervals: 0.5.

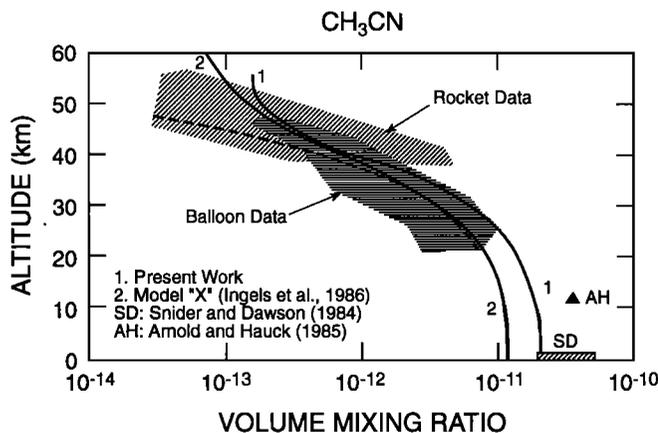


Fig. 2b. Comparison of vertical distribution of methyl cyanide calculated at 45°N by the two-dimensional model with all available observational data. A model profile obtained by Ingels *et al.* [1986] is also shown.

parameterization given by Heaps [1978] for solar maximum conditions and described more precisely by Brasseur and Solomon [1986]. The first ion formed in this region is  $O_2^+$  which reacts with  $O_2$  to form  $O_4^+$ . Subsequently, other ions, namely,  $O_2^+H_2O$ ,  $H_3O^+OH$ , etc., are formed before reacting to the terminal ion  $H^+(H_2O)$  which is the first member of the proton hydrate family. The second proton hydrate is formed from  $H_3O^+OH$  and  $H^+(H_2O)$ . From  $O_2^+$  up to  $H^+(H_2O)_2$  all the reaction paths and their rate coefficients are known with good accuracy from laboratory studies. Since  $H^+(H_2O)$  and  $H^+(H_2O)_2$  are not the major PH ions, we have taken a simplified approach by taking  $H^+(H_2O)_n$  as the sum of all other remaining proton hydrates. This  $H^+(H_2O)_n$  is formed from  $H^+(H_2O)_2$  with a reaction rate (R9) (see Figure 3), whose value is considered to

be the same as used earlier by Beig and Chakrabarty [1988]. There could be several reaction paths between the PH and the NPH. In the present work we assume NPH to be the sum of all the nonproton hydrates formed from  $H^+(H_2O)_n$  by the reaction with  $CH_3CN$  through a single reaction channel whose rate is (R10), which is given by  $(R10) = K (CH_3CN)$ . Different case studies were made by taking different values of rate coefficient  $K$  and its effect on ion composition is examined.

The loss of ions in the stratosphere is mainly by mutual recombination between positive and negative ions. It is now believed that the two body recombination ( $\alpha_2$ ) processes dominate in the upper stratosphere above about 40 km and the three-body recombination ( $\alpha_3$ ) processes dominate in the lower part. Several experimental as well as theoretical values of  $\alpha_2$  and  $\alpha_3$  are available [Rosen and Hofmann, 1981; Bates, 1982]. In the present work the values of  $\alpha_2$  and  $\alpha_3$  are adopted similar to the one used earlier by Arijs and Brasseur [1986] and Beig and Chakrabarty [1988] in their model studies.

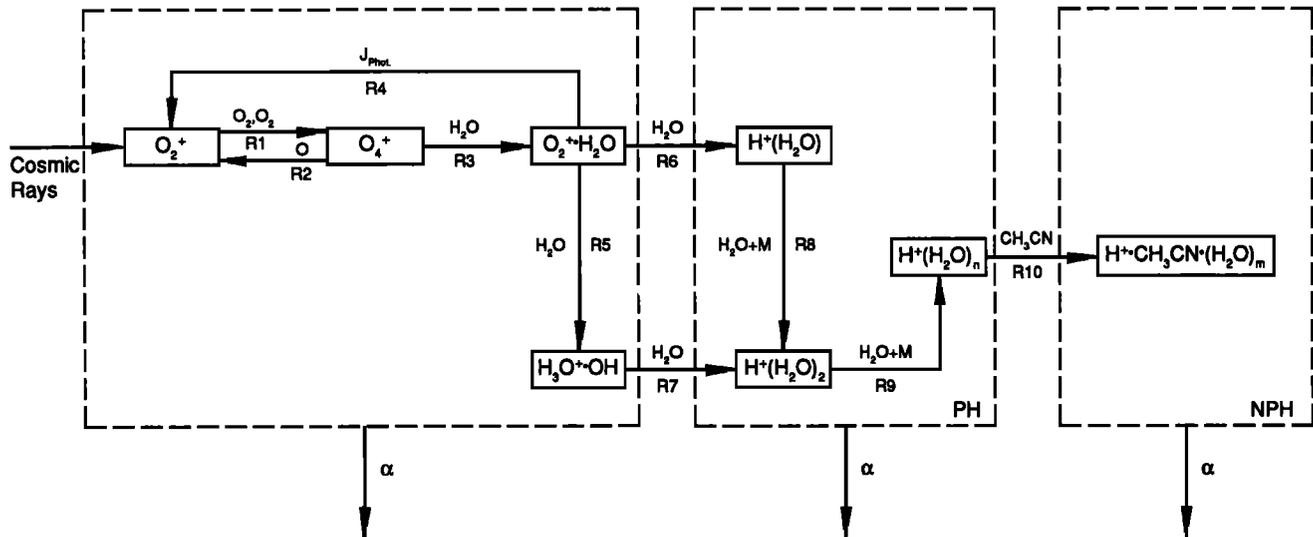
#### 4. MODEL RESULTS AND DISCUSSION

The continuity equations of all the ions (shown in Figure 3) are written and solved simultaneously for the steady state conditions. The sum of all the positive ions is taken as equal to the total negative ion for charge neutrality. The ion scheme is coupled with the two-dimensional meridional model for the altitude range from 15 to 55 km. Calculations were done at an interval of 1 km. In this first case the most commonly used value of rate coefficient  $K = 1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  is used. This value of  $K$  is reported by Fehsenfeld *et al.* [1978] and later used by Beig and Chakrabarty [1988] in their model study.

Figure 4 shows the meridional distribution of total positive ion density obtained in this work. The total number density of positive ions at the tropical latitudes is lower than at other latitudes. The ion density increases with latitude from the equator toward the poles. This variation in ion density is due to the production rate by galactic cosmic rays which is minimum at the equator and maximum near the poles. The total positive ion density varies from  $5.0 \times 10^3 \text{ cm}^{-3}$  to about  $1 \times 10^3 \text{ cm}^{-3}$  for the altitude region from the 15 to about 50 km. This value of ion density is in good agreement with the observational results obtained at different latitudes by different authors [Rosen *et al.*, 1985; Beig *et al.*, 1989].

The meridional distribution of total proton hydrates and nonproton hydrates obtained in this work is shown in Figures 5a, 5b. It is clear from this figure that the distribution of PH and NPH ions is almost identical for both northern and southern hemispheres and is not influenced by the season. It can be seen from Figure 5a that the concentration of proton hydrates is higher near the poles through about  $\pm 60^\circ$  latitude, compared to other latitudes. There exists an appreciable variation of PH with height in this latitude region. The value of PH density starts to fall down from  $\pm 60^\circ$  toward the equator. Its density becomes minimum at the equator. The PH ions do not show much variability with altitude in the tropical region.

Figure 5b shows the latitudinal distribution of NPH. It is found that the NPH ions show less variability with latitude compared to PH ions. In general, concentrations of NPH ions start to decrease with increasing altitude. It is interesting to notice that the NPH ions at the tropics show a dip for the altitude region of 15 to 30 km. In this height region the value of NPH decreases toward the equator. However, this dip in NPH near the equator corresponds to the low value of total positive



$$\begin{aligned}
 R1 &= 2.4 \times 10^{-30} (300/T)^{3.2} [O_2]^2 & R6 &= 3.2 \times 10^{-10} [H_2O] \\
 R2 &= 3.0 \times 10^{-10} [O] & R7 &= 3.2 \times 10^{-9} [H_2O] \\
 R3 &= 2.2 \times 10^{-9} [H_2O] & R8 &= 3.5 \times 10^{-27} (300/T)^{2.0} [H_2O] [M] \\
 R4 &= 0.6 = \text{Photodetachment} & R9 &= R8 \\
 R5 &= 1.9 \times 10^{-9} [H_2O] & R10 &= K [CH_3CN]
 \end{aligned}$$

[M] = Neutral number density  
 T = Temperature  
 K = Rate coefficient (see text)

Fig. 3. Simplified positive ion scheme adopted in this work.

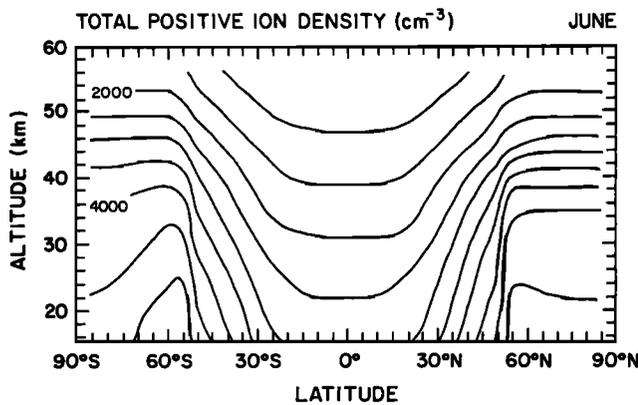


Fig. 4. Meridional distribution of total ion density ( $\text{cm}^{-3}$ ) calculated in the model. Contour intervals:  $500 \text{ cm}^{-3}$ .

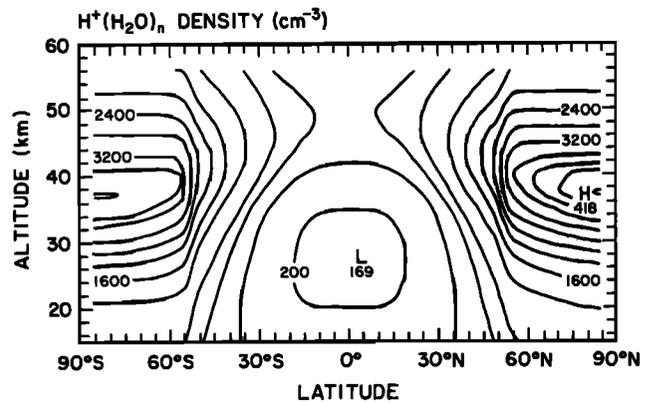


Fig. 5a. Same as Figure 4 but for the sum of proton hydrates.

ion density which is due to the low cosmic ray production rate at low latitudes. Above about 30 km the distribution of NPH ions shows a slight but significant increase at the tropics compared to other latitudes.

Figure 6 shows the ratio of NPH ions to PH ions, as a function of altitude and latitude. This figure shows the crossover points of PH over NPH for different latitudes. The following interesting points emerge from Figure 6. (1) It is clear that the altitude of the crossover point (highest contour shown in the figure) is lowest at the poles and highest at the equator. As we go away from the poles toward the equator, the height of the crossover point starts increasing and becomes maximum at the equator (about 46 km). (2) The pattern of

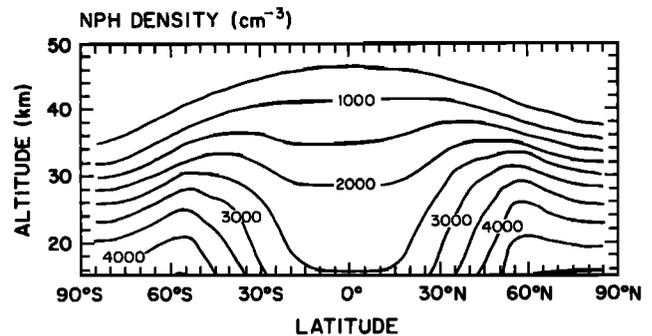


Fig. 5b. Same as Figure 5a but for the sum of nonproton hydrates. Contour intervals:  $500 \text{ cm}^{-3}$ .

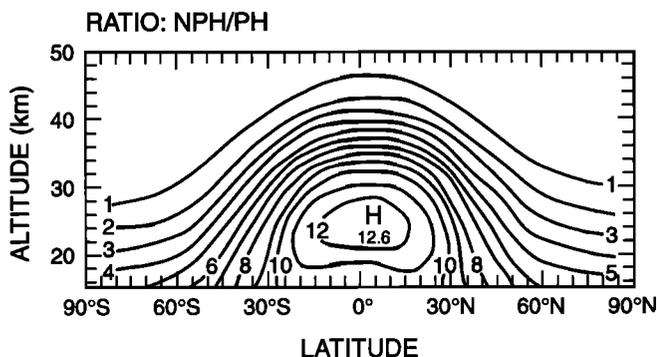


Fig. 6. Ratio of nonproton hydrates over proton hydrates calculated as a function of latitude and altitude. Contour intervals: 1.

NPH/PH ratio appears to be almost similar in both hemispheres. However, at the south pole the crossover point in June is at about 27 km, whereas at the north pole it reaches at about 30 km. (3) The crossover point is at 37 km near 45°N which is consistent with the observational results which are available only for this latitude region [Arijs *et al.*, 1983; Beig and Chakrabarty, 1988]. (4) The variation in the altitude of the crossover point with latitude is largely due to the meridional variation in the distribution of methyl cyanide. As mentioned earlier, the NPH ions are formed by the reaction of PH ions with CH<sub>3</sub>CN. The high value of CH<sub>3</sub>CN near the equator makes the conversion of PH to NPH faster and a dominant process, as a result of which NPH ions dominate up to about 46 km. At the poles, due to the low concentration of CH<sub>3</sub>CN, the conversion process of PH to NPH becomes insignificant above about 25 km.

To compare our model results with the only available observational data at 44°N, the percentage abundances of proton hydrate and nonproton hydrate ions are plotted as a function of altitude in Figure 7 for 45°N. In this figure, profiles 1a and 1b represent the calculated percentage abundance of PH and NPH ions, respectively. The observational results of PH and NPH obtained to date by two groups, i.e., Belgian Institute for Space Aeronomy (BISA) [e.g., Arijs *et al.*, 1983] and Max-Planck-Institut für Kernphysik Heidelberg (MPIH), [e.g., Arnold *et al.*, 1978] are also shown in this figure. Profile 2 represents the percentage abundance of NPH ions as obtained by Arijs and Brasseur [1986] from their model study. This profile is derived from an average reaction rate and a global CH<sub>3</sub>CN emission of  $4.7 \times 10^{10}$  g/yr. There appears to be a lot of scatter in the observational data. The uncertainty in experimental data due to observational error is estimated to be about 20–30% [Ingels *et al.*, 1986]. However, it is clear from Figure 7 that the abundance of NPH ions start to dominate and a crossover is seen somewhere between 35 and 40 km. Calculated profiles are in reasonably good agreement with the observed data but seem to be slightly lower compared to the model profile 2, although in good qualitative agreement. It is also clear that the crossover point of NPH and PH occurs around 37.5 km for the present case. There are no observational data available for ion composition below about 20 km. Hence no comparison can be made. However, our model profile shows that NPH ions are the predominant ions even at lower altitude.

The ratio of nonproton hydrate to proton hydrate obtained for 45°N in the present work is shown in Figure 8. Also shown in Figure 8 are the observational results available from two experimental groups viz BISA and MPIH. Model profiles obtained by Beig and Chakrabarty [1988] using a similar

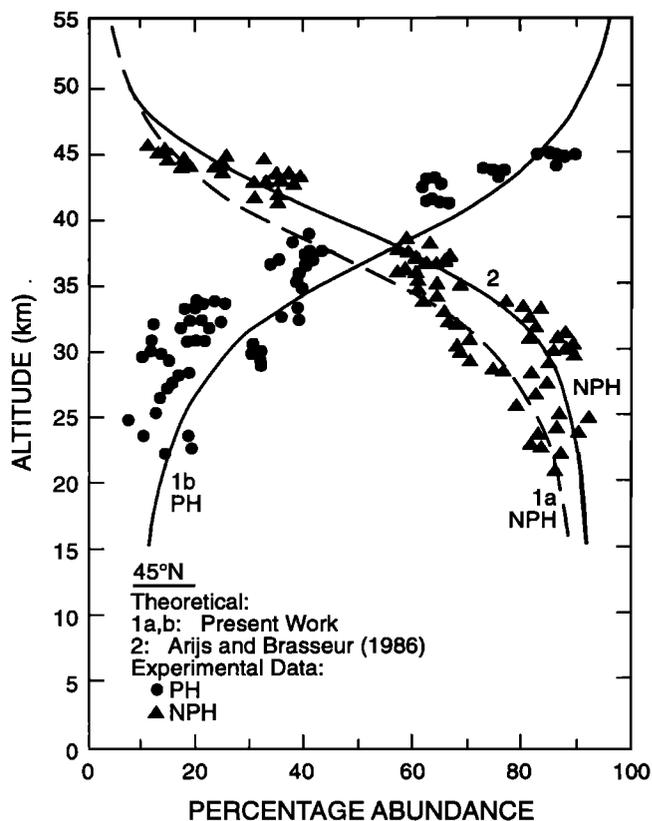


Fig. 7. Percentage abundance of proton hydrates (PH) and nonproton hydrates (NPH) as a function of altitude at 45°N. Calculated values are compared with experimental data. Values of NPH abundance derived by Arijs and Brasseur [1986] are also shown.

scheme are also plotted. There is a lot of scatter in the experimental data. The MPIH results appear to be somewhat higher than the BISA results. The ratio becomes equal to 1 at about 38 km which represents the crossover point of PH and NPH. The present profile is in good agreement with the previously obtained model profile 2.

Figure 9 represents for different latitudes the altitude of the crossover point as a function of the rate coefficient ( $K$ ) for the conversion of PH to NHP.  $K$  is defined as



$$K = R_{10}[\text{CH}_3\text{CN}]$$

As we notice from Figure 9, the crossover point becomes higher as the value of rate coefficient increases. Again, one notes that the height of the crossover point is maximum at the equator and decreases toward the poles. There appears to be a slight difference in the profile for north and south poles. The height of the crossover point at the south pole is about 2 km more than at the north pole in June.

## 5. CONCLUSIONS

A major requirement for a model study of the ionic composition of the middle atmosphere is information on the distribution of minor neutral constituents for incorporation in ion chemical schemes. In this paper an attempt has been made to achieve this goal. The distribution of minor neutral

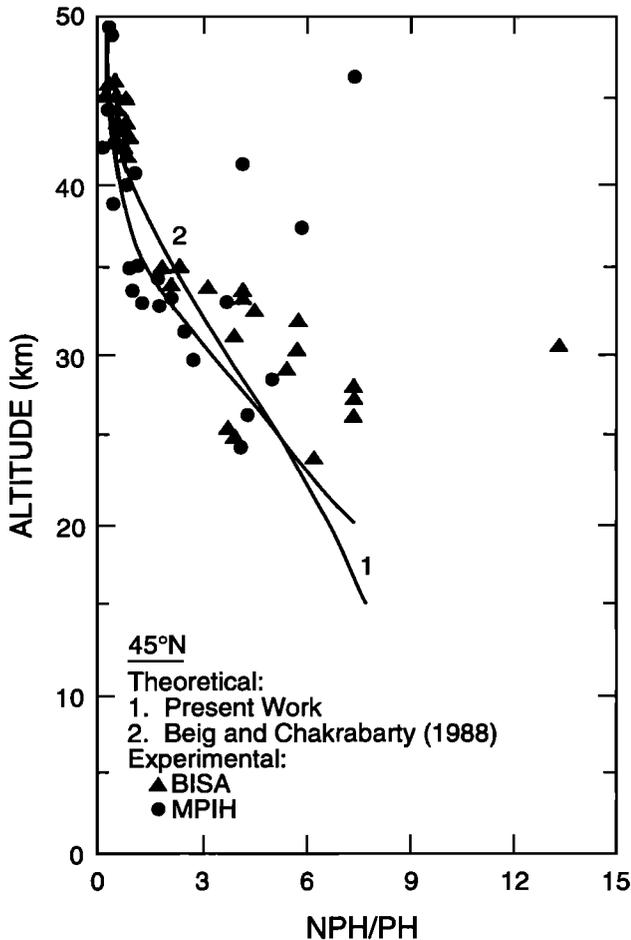


Fig. 8. Ratio of nonproton hydrates (NPH) over proton hydrate (PH) concentrations calculated as a function of altitude at 45°N. These results are compared with observational data reported by two groups (BISA and MPIH; see text) and with a model study by *Beig and Chakrabarty* [1988].

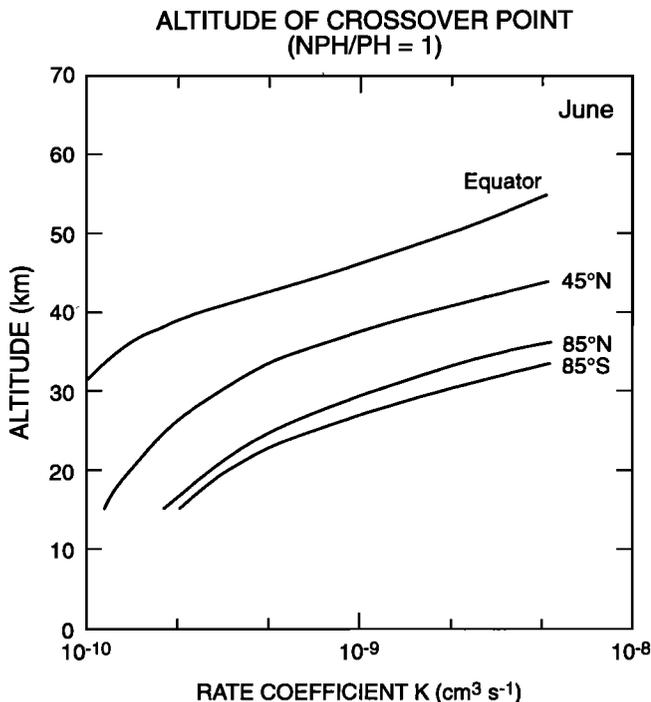


Fig. 9. Altitude at which the concentrations of proton hydrates (PH) and nonproton hydrates (NPH) become equal, for different latitudes and different PH to NPH conversion rates. June conditions.

constituents used in this study has been calculated from a comprehensive two-dimensional model. In the absence of accurate values of reaction rates for making detailed calculations, a simplified ion chemical scheme has been used, which involves minimum assumptions.

The model results reproduce the main features of ion composition measurements obtained at middle latitudes. Ion densities calculated for other latitudes need to be confirmed by observational data. Consistently with observational data, the model suggests that the positive ion composition is driven by methyl cyanide in the lower stratosphere and water vapor in the upper stratosphere. The height of the crossover point of PH over NPH varies strongly with latitude. This crossover point is also very sensitive to the conversion rate of PH to NPH necessitating laboratory studies. Finally, it is stressed that reference models of ions below the stratopause should include a latitudinal dependence, which needs to be confirmed by observational data.

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