

SHORT PAPER

PHOTOLYSIS OF METHANE AND THE IONOSPHERE OF URANUS

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Abstract

Photochemical calculations for Uranus predict an extensive region of condensation of acetylene, ethane and methane in the vicinity of the temperature inversion layer. This could explain why ethane was not detected on Uranus, unlike Neptune which has a much warmer inversion layer. Subsequent snow-out of the condensibles is expected to result in reduced visibility in the troposphere. Ionospheric calculations for the equatorial region to be probed by Voyager, indicate peak electron concentrations on the order of $5 \times 10^3 \text{ cm}^{-3}$, if dynamical effects are important. Upper limit to the electron peak is $3 \times 10^4 \text{ cm}^{-3}$. Exospheric temperatures as high as 200-250K are conceivable.

1. INTRODUCTION

The knowledge of methane (CH_4) distribution in the atmosphere of Uranus is essential for interpreting recent observations of the Uranian Lyman-alpha emission (Fricke and Darius, 1982; Clarke, 1982; and Durrance and Moos, 1982); for understanding the atmospheric radiative transfer (Courtin, *et al.*, 1978; Wallace, 1980; and Appleby, 1980); and for modeling the structure of the lower ionosphere (Atreya and Donahue, 1975a and 1975b). Ground-based observations have indicated an enrichment of methane on Uranus relative to the solar C/H ratio (Wallace, 1980). This enrichment, however, is applicable to the deep troposphere where sublimation of methane is non-existent due to the relatively high temperatures. Above the troposphere, however, the distribution of methane is controlled by photochemistry, including diffusion. This paper deals with: (i) photolysis of methane, which leads to the formation of ethylene (C_2H_4), ethane (C_2H_6), and acetylene (C_2H_2); possible condensation and snow-out of the products is considered; (ii) lower ionosphere, where hydrogen ions are converted to short-lived hydrocarbon ions, (iii) upper ionosphere, for the sake of completeness and to set the scene for receipt and interpretation of the radio occultation observations on Voyager/Uranus in January, 1986.

2. METHOD AND ASSUMPTIONS

The chemical scheme for the methane photolysis program is the same as we used earlier for Jupiter (Atreya, *et al.*, 1981), and Saturn (Atreya, 1982) since that scheme reproduced the Voyager measurements satisfactorily. Briefly, CH_4 is dissociated by the solar photons at wavelengths shortward of 1600\AA resulting eventually in the formation of C_2H_4 and C_2H_6 . Both C_2H_4 and C_2H_6 would recycle some of the CH_4 back, and would also form C_2H_2 . Although C_2H_2 undergoes photodissociation and three-body reactions, it is readily recycled back to C_2H_2 and is thus quite stable in the Uranian atmosphere (unless, of course, if it undergoes condensation, as discussed later). The chemical scheme for the ionosphere is the same as we have used for Jupiter and Saturn (see, e.g., Atreya and Donahue, 1976 and 1982; and Atreya, *et al.*, 1983). The major gases H_2 , He, and H are ionized by the solar EUV photons of wavelengths shorter than 804\AA , 911\AA and 504\AA , respectively. Dissociative ionization of H_2 provides the dominant source of the major topside ion H^+ . The possibility of a molecular ion in the topside is explored. Below the peak, H_3^+ , and well below the peak, the hydrocarbon ions (such as C_2H_5^+ , CH_5^+ , C_3H_3^+ , C_4H_9^+ , etc.) are formed following ion-molecule charge exchange. All terminal ions are removed by electron recombination. Since the main purpose of this paper is to simulate the structure for the Voyager observation regions, only solar EUV ionization is considered as the occultation measurements will be done at 2° and 6° latitudes. One dimensional, steady state solutions are obtained by solving a set of non-linear partial

differential equations for both the photolysis and the ionospheric products (see Banks and Kockarts (1973) for a general description of the continuity equations). Certain assumptions about the temperature structure, atmospheric composition, vertical mixing, and the solar flux had to be made, and they are discussed below.

a. Temperature structure. Radiative-convective models of Wallace (1980) and Courtin, et al. (1978) give a temperature of between 50 and 55K at the tropopause, or the inversion layer where the atmospheric pressure is between ~10 and ~100mb. Recently, Tokunaga, et al. (1983) have deduced an inversion temperature of approximately 55K from the 17.8 μ m and 19.6 μ m measurements. Because of considerable uncertainties in the various models, we have considered both extremes of the inversion temperature in our calculations, and the 55K at 100mb value is assumed to represent the 'nominal' case.

From the ground-based stellar occultation observations in 1977, Dunham, et al. (1980) deduced a mean temperature of 95K between 0.3 μ b and 30 μ b, with perhaps up to 30K possible excursion about the mean value. The immersion data are for latitudes quite similar to those for the Voyager/Uranus radio occultations. No temperature measurements for the region between the inversion layer and 30 μ b are available. Since most of the photolysis occurs high in the atmosphere, where the temperature would be close to the stellar occultation value, we have assumed an average photolysis region temperature of 95K. The stellar occultations of August, 1980 done at 18° and -26° latitudes give a temperature of 154±15K (French, et al., 1983), indicating either a temporal or latitudinal variation in the energy budget. We shall, therefore, present also the photolysis results for 18° latitude, and 154K mean temperature to demonstrate the effect of latitude and temperature on the hydrocarbon distributions.

The temperature in the ionospheric region is not expected to be substantially greater than that in the abovementioned region of the stellar occultation. This is due to the fact that the solar EUV at Uranus is not expected to raise the temperature substantially above that at the homopause, and the charged particle precipitation would be confined to the high latitudes. If the observed Lyman-alpha emission (see e.g., Clarke, 1982) were of auroral origin, we calculate the total energy deposition of the order of 10¹¹ Watts (see also Hill, et al., 1983). Even if this energy were spread over the planet with a 100% efficiency, it would amount to a flux of approximately 0.02 erg cm⁻² s⁻¹. A simplified solution of the heat conduction equation shows that this amount of energy is insufficient for heating the thermosphere to a large degree. A 100 to 150K rise in temperature is conceivable, and its effect on the ionospheric profile will be addressed later.

b. Atmospheric composition. The most important gas whose abundance we must know for the present calculations is methane. For the abovementioned range of inversion temperatures, the CH₄-volume mixing ratios dictated by its saturation vapor pressure, (Karwat, 1924) at the 100mb atmospheric pressure level are: 2.4x10⁻⁵ and 2.2x10⁻⁴ for temperatures of 50K and 55K respectively.

Assuming that there is no supersaturation, the CH₄-mixing ratios cannot be greater than these values at altitudes above the inversion layer. The mixing ratios of the other hydrocarbons C₂H₆, C₂H₂, C₂H₄, etc. at the 100mb level simply serve as boundary values since methane photolysis higher in the atmosphere would govern their abundances. There is no strong evidence of a significant enrichment of helium relative to its solar abundance (Courtin, et al., 1978). In any event, helium plays a minor role both in the methane photolysis and the ionospheric schemes. We take He/H₂=11% by volume, same as the solar value.

c. Vertical mixing. Unlike the situation with the other outer planets, it is not possible to exploit the current observations of Uranus Lyman-alpha emission rate to arrive at an estimate of the homopause value of the eddy diffusion coefficient. This is because one does not know precisely the auroral contribution to the observed Lyman-alpha from Uranus. In view of the fact that Uranus does not seem to possess an internal heat source (Lowenstein, et al., 1977), that it receives 1/400 of the solar energy incident on the earth, and that the globally averaged auroral energy input is insignificant, it is difficult to imagine that Uranus would exhibit large vertical mixing. For our calculations, we have assumed a nominal value of K=10⁶ cm² s⁻¹ at the homopause, which is representative also of Jupiter and the earth at corresponding levels. We also discuss the effect of lower and higher values of K on our calculations. After Jupiter and Saturn (Atreya, et al., 1981; Atreya, 1982), $K \propto M^{-1/2}$ variation is assumed, where M is the atmospheric number density.

d. Solar flux. Voyager/Uranus encounter in January, 1986, is at a period of solar minimum flux. Recent measurements done in May, 1982, and January, 1983, by Mount and Rottman (1983) indicate that the solar fluxes below 1900\AA have already dropped to their solar minimum values. In our calculations we assume the fluxes corresponding to the last solar minimum, after Hinteregger (1981) since he covers the entire wavelength range of interest here. The fluxes have been reduced for the distance of Uranus ($\sim 19.2\text{AU}$), and adjustments for the solar zenith angles and latitudes of the Voyager radio occultations (JPL, 1983) have been made according to the formulation of Levine, *et al.* (1977).

The other useful parameters in the calculations are: $g=800\text{ cm s}^{-2}$; $R_U=25,400\text{km}$; inclination of equator to orbit= 98° . Exact values of these parameters are not known; however, a change of the order of 10% in 'g' and ' R_U ' would have little effect on the results.

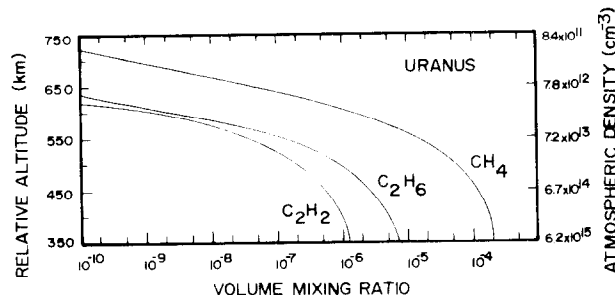


Fig. 1. Volume mixing ratios of CH_4 , C_2H_2 and C_2H_6 as a function of altitude (left ordinate) for the 'nominal' case. Here, eddy mixing coefficient at the tropopause, $K_0=10^3\text{ cm}^2\text{ s}^{-1}$, at the homopause, $K_h=1.4 \times 10^6\text{ cm}^2\text{ s}^{-1}$; temperature at the inversion level, $T_{\text{inv}}=55\text{K}$, in the photolysis regime, $T_{\text{photo}}=95\text{K}$; latitude= 2° ; and solar minimum flux. The results for 6° latitude are virtually indistinguishable. The atmospheric densities (right ordinate) correspond to the altitudes shown on the left coordinate. The altitudes are referenced to the 100mbar (inversion layer) level. Add approximately 100km to obtain altitudes above the 1-bar level.

3. RESULTS AND DISCUSSION

We show in Fig. 1 distribution of CH_4 , C_2H_6 , and C_2H_2 for the nominal case. Photolysis of CH_4 is virtually non-existent below 350km. If one were to assume that the mixing ratios of C_2H_2 and C_2H_6 at the inversion level (55K, 100mbar) are the same as those at the lowest boundary (350km) in Fig. 1, one would discover that condensation of C_2H_2 and C_2H_6 would be a distinct possibility. For example, the calculated C_2H_2 partial pressure at the 100mbar level would be 10^{-4}mb , while its saturation vapor pressure there (at 50 or 55K) is less than 10^{-12}mb . No reasonable degree of supersaturation could permit the calculated C_2H_2 to stay in the vapor phase. Hence condensation and subsequent snow-out of C_2H_2 in the Uranus atmosphere is a virtual certainty. Depending on the vertical mixing, C_2H_2 mixing ratio at the 100mbar level could be lower than that at the 350km, however an 8 orders of magnitude decrease is unlikely. The calculated C_2H_6 partial pressure at the 100mb level is 10^{-3}mb , while its saturation vapor pressure there (55K) is only 10^{-5}mb . Without supersaturation, or a decrease in C_2H_6 near the 100mbar level, C_2H_6 is likely to condense also. For the inversion layer higher in the atmosphere ($\sim 10\text{mb}$ level), condensation of C_2H_6 is still expected to occur between 10 and 100mb region. We suggest that possible condensation of C_2H_6 could explain why C_2H_6 has not been detected in the IR spectrum of Uranus at $12.2\mu\text{m}$ (Macy and Sinton, 1977), while it is definitely present on Neptune which has a much warmer thermal inversion layer than Uranus. If the CH_4 mixing ratio is indeed as high as 1×10^{-2} (Wallace, 1980), one cannot escape the conclusion that CH_4 will definitely condense at the 100mbar level, or even higher in the atmosphere. Even if the CH_4 mixing ratio were close to solar (7×10^{-4}), its partial pressure would still be greater than the saturation vapor pressure around the 10mb level for 50 or 55K inversion temperature. Thus, condensation of CH_4 is expected to occur in the vicinity of the cold-trap. C_2H_4 would not condense because of its low mixing ratio. It should be pointed out that the same conclusions on C_2H_2 , C_2H_6 , CH_4 and C_2H_4 condensation are reached for the various cases discussed in Figure 2.

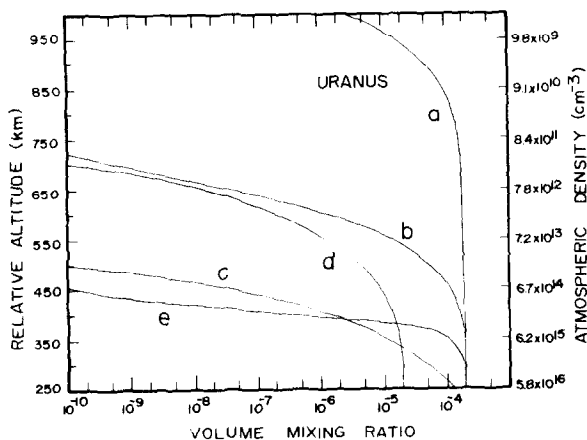


Fig. 2. Variation of CH_4 volume mixing ratio with: (i) K_{H} : curves 'a', 'b', and 'c', where $K_{\text{H}}=1.3 \times 10^{10} \text{ cm}^2 \text{ s}^{-1}$, $1.4 \times 10^6 \text{ cm}^2 \text{ s}^{-1}$, and $1.3 \times 10^4 \text{ cm}^2 \text{ s}^{-1}$ respectively. Curves 'a', 'b', and 'c' have $T_{\text{inv}}=55\text{K}$, $T_{\text{photo}}=95\text{K}$, and latitude 2° . Curve 'b' is termed as the 'nominal' case; (ii) T_{inv} : curve 'd', where $T_{\text{inv}}=50\text{K}$ so that $[\text{CH}_4]/[\text{H}_2]=2.2 \times 10^{-9}$ at the 100mb level. Other parameters are same as in curve 'b'; and (iii) latitude: curve 'e', where the latitude is 82° which represents the sub-solar point; the North-pole is pointing almost directly at the Sun in this geometry, and other parameters are same as in curve 'b'. Altitude and density scales in this figure are same as in Figure 1.

The variation of CH_4 -mixing ratio with vertical mixing, inversion temperature and latitude is shown in Fig. 2. As expected, vertical mixing is extremely important in determining the distribution of the hydrocarbons (compare Fig. 2, curves 'a', 'b' and 'c'). A lower temperature (50K) at the inversion layer gives a lower CH_4 mixing ratio at all altitudes (compare Fig. 2, curve 'd' with curve 'b'). Greater solar flux available near the poles is responsible for a dramatically compressed photolysis region (compare Fig. 2 'e' and 'b').

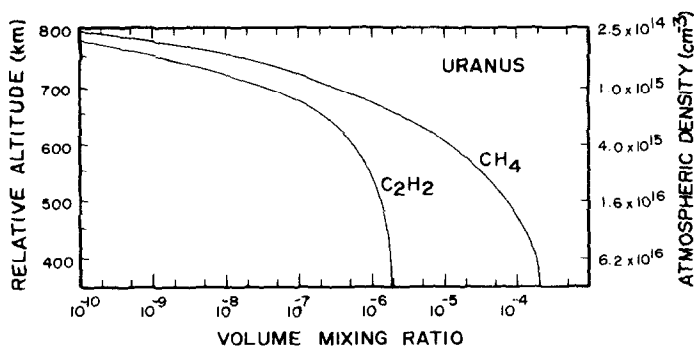


Fig. 3. Volume mixing ratios of CH_4 and C_2H_2 for $K_0=1.5 \times 10^2 \text{ cm}^2 \text{ s}^{-1}$; $K_{\text{H}}=3 \times 10^4 \text{ cm}^2 \text{ s}^{-1}$; $T_{\text{inv}}=55\text{K}$, $T_{\text{photo}}=154\text{K}$; and latitude 18° . Altitude and density scales are same as in Fig. 1.

We show in Fig. 3 the calculations for the 18° latitude, with $T_{\text{photo}}=154\text{K}$, and $K_{\text{h}}=3\times 10^4 \text{ cm}^2 \text{ s}^{-1}$ to simulate the situation proposed for the 1980 stellar occultation (French, *et al.*, 1983). (Note that $K_{\text{h}}=3\times 10^4$ is not a measured or deduced value for Uranus; indeed such low values of K_{h} have not yet been encountered on any planet). The calculated CH_4 and C_2H_2 mixing ratios at altitudes relevant to the stellar occultation (atmospheric density $\sim 10^{14} \text{ cm}^{-3}$) are each less than 10^{-10} . French, *et al.* (1983) have suggested upper limits of 6×10^{-5} and 5×10^{-7} for CH_4 and C_2H_2 respectively. These upper limits are close to the values we calculate at $\sim 10^{14} \text{ cm}^{-3}$ level in the nominal case (Fig. 1), where $K_{\text{h}}=10^6 \text{ cm}^2 \text{ s}^{-1}$, and $T_{\text{photo}}=95\text{K}$. To illustrate the effect of changing the photolysis region temperature on the methane distribution, we have calculated a case with $T_{\text{photo}}=95\text{K}$ while holding all other parameters same as for Fig. 3. We find that at an atmospheric density level of $6\times 10^{15} \text{ cm}^{-3}$, e.g., $\text{CH}_4/\text{H}_2=4\times 10^{-5}$ for $T_{\text{photo}}=95\text{K}$, rather than 2×10^{-5} with $T_{\text{photo}}=154\text{K}$. This difference becomes greater at lower atmospheric density levels, e.g., at an atmospheric density level of $3\times 10^{14} \text{ cm}^{-3}$, $\text{CH}_4/\text{H}_2=3\times 10^{-8}$ for $T_{\text{photo}}=95\text{K}$, and it is 2×10^{-9} with $T_{\text{photo}}=154\text{K}$.

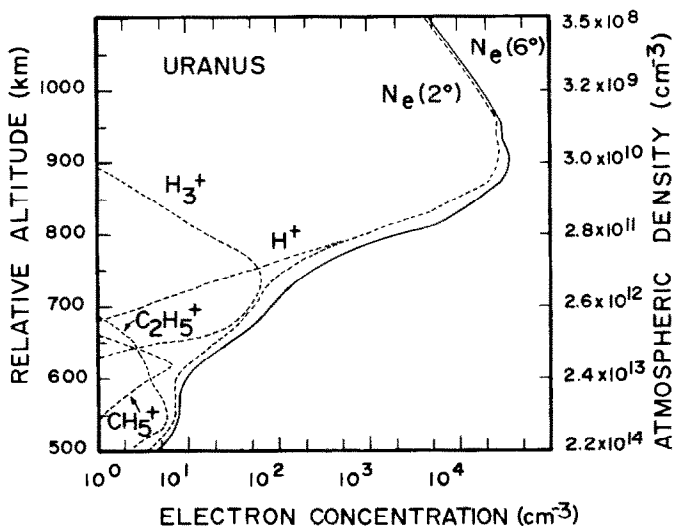


Fig. 4. Photochemical equilibrium electron and ion concentrations for the Voyager/Uranus radio occultation points located at 2° and 6° latitudes. The atmospheric model is same as in Figure 1 ('nominal' case). To avoid cluttering, ion concentrations are shown only for the 6° case. See text for the expected electron concentrations. Altitude and density scales are same as in Figure 1.

The ionospheric distributions corresponding to the Voyager/Uranus radio occultation geometries are shown in Fig. 4. The hydrocarbon ions have low concentrations in the nominal case presented in this figure. The topside electron concentrations remain unaffected unless $K_{\text{h}} \geq 10^{10} \text{ cm}^2 \text{ s}^{-1}$ -- an unacceptably high value. Conversion of the topside H^+ ions to a molecular ion (such as H_3^+ , Atreya, *et al.*, 1983), other than the hydrocarbons is a possibility which should be explored. The thin rings of Uranus, however, are not expected to influence the ion distribution. The peak electron concentration of $(2-3)\times 10^4 \text{ cm}^{-3}$ shown in this figure represents the upper limit for solar minimum. As explained earlier, an exospheric temperature of 200-250K is conceivable. This would result in twice the scale height in the topside than shown in Fig. 4. The change in electron concentration due to the temperature dependence of the radiative recombination rate constant of H^+ (Bates and Dalgarno, 1962) would, however, be small. All dynamical effects, such as ion transport and ion drift, would tend to redistribute the ions and reduce the peak electron concentration. Experience with Voyager observations of Jupiter and Saturn suggests that the peak electron concentration at Uranus would be lower than the value in Fig. 4, and is expected to be on the order of $5\times 10^3 \text{ cm}^{-3}$. The ionosphere in the

high latitudes (not probed by Voyager) is expected to be modified by the pole-on magnetospheric geometry.

4. CONCLUSIONS

(i) Photolysis calculations indicate condensation of C_2H_2 , C_2H_6 and CH_4 near the inversion layer; and (ii) Peak electron concentrations at 2° and 6° latitudes would be on the order of $5 \times 10^3 \text{ cm}^{-3}$, if dynamical effects are important. The upper limit to the peak electron concentration, however, is $3 \times 10^4 \text{ cm}^{-3}$. Exospheric temperatures of the order of 200-250K are plausible.

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