ISO OBSERVATIONS OF C_2H_2 ON URANUS AND CH_3 ON SATURN: IMPLICATIONS FOR ATMOSPHERIC VERTICAL MIXING IN THE VOYAGER AND ISO EPOCHS, AND A CALL FOR RELEVANT LABORATORY MEASUREMENTS

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ABSTRACT

In October 1996, ISO/SWS recorded the spectra of Uranus in the 7-16.5 μm. range and detected the spectral signatures of acetylene (C_2H_2). Interpretation of the C_2H_2 density profile with photochemical models leads to a value of $(5 - 10) \times 10^3$ cm^{2}s^{-1} for the eddy diffusion coefficient (K_h) at the Uranus homopause, which for these limits of K_h corresponds to 354 km (0.037 mb) and 390 km (0.02 mb) above the 1-bar level. The eddy coefficient derived from these globally averaged observations is found to be in agreement with the values obtained by Voyager for the equatorial-low latitudes ten years earlier. The ISO-Voyager consistency in K_h indicates that whatever little manifestable internal energy Uranus possesses may still be adequate and responsible for controlling the behaviour of vertical mixing in its visible atmosphere, and that the dynamical behaviour of the upper atmosphere is fairly uniform over the planet. In December 1997, methyl radicals (CH_3) were also detected by ISO/SWS in the atmosphere of Saturn. The derived stratospheric column abundance of CH_3, $(1.5-7.5) \times 10^{13}$ cm^{-2}, is about a factor of 10 smaller than the predictions of methane photochemical models, however. The discrepancy could be explained by one of two means: either the value of the eddy diffusion coefficient used in the models — the Voyager value — is too high by at least a factor of 100, or the rate constant for the self-reaction loss of CH_3 is too low by at least a factor of 10. It is argued that K_h could not possibly be reduced so drastically from the Voyager epoch. Instead, we believe the source of the discrepancy between the ISO derived CH_3 and the model calculations lies in the poor knowledge of laboratory chemical kinetics data on certain CH_3 loss reactions, which has serious implications for the interpretation of observations of atmospheres of the giant planets and Titan.

1. ISO DETECTION OF C_2H_2 ON URANUS: ATMOSPHERIC VERTICAL MIXING

The Short Wavelength Spectrometer on the Infrared Space Observatory (ISO/SWS) detected unambiguously in 1996 the ν_5 band signature of acetylene (C_2H_2) centered at 13.7 μm. (Encrenaz et al. 1998). C_2H_2 is one of the principal stable products of methane photochemistry, hence its distribution can be used to determine the physico-chemical properties of the giant planet atmospheres (Atreya, 1986). In particular, the strength of vertical mixing, which is characterized by the eddy diffusion coefficient, K, can be determined by comparing the model abundances with those measured. K is treated as a free parameter in the methane photochemical models. A simplified chemical scheme showing the pathways leading to the formation of acetylene and other stable hydrocarbons in the giant planet atmospheres is shown in Fig. 1. Nearly 92% of all methane photolysis takes place at the wavelength of Lyman-α (121.6 nm) because of the large solar flux at this wavelength. The quantum efficiency of the formation of some of the products of CH_4, particularly CH_3, has been measured most recently at Ly-α by Mordaunt et al. (1993). Combining these data with earlier lab measurements leads to a quantum efficiency of 0.41 for CH_3, 0.1 for CH, 0.28
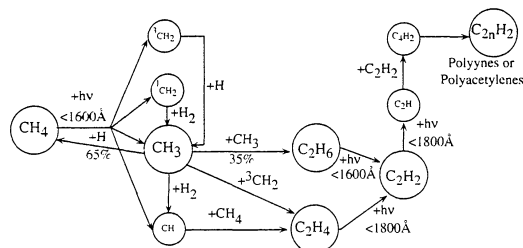

Figure 1. CH_4 photochemistry of the giant planets (after Atreya et al. 1997)

Key words: Saturn; Uranus; Titan; giant planets; photochemistry; atmospheric vertical mixing.
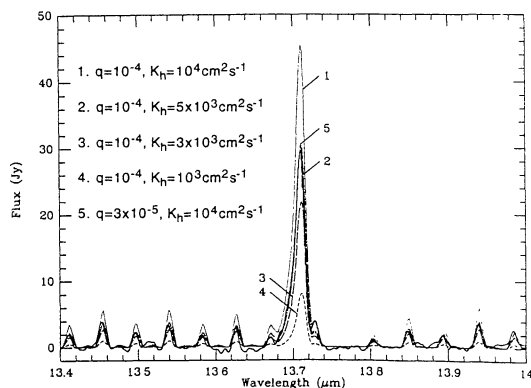
Figure 2. Synthetic spectra (with various combinations of K_h and q_{CH_4}) fitted to the ISO C_2H_2 observation of Uranus (after Encrenaz et al. 1998).

Figure 3. Illumination of Uranus in orbit around the Sun.

for $^1CH_2$ and 0.21 for $^3CH_2$ (Romani 1996; Bishop et al. 1998). Voyager data indicated that the mixing ratio of CH_4 at the tropopause of Uranus, q_{CH_4}, lies in the $(0.3 - 1) \times 10^{-4}$ range (Bishop et al. 1990). Using these values of q_{CH_4} and by varying K, one can obtain various distributions of C_2H_2, which can then be used to construct synthetic spectra for comparison with the one measured by ISO/SWS. Fig. 2 shows such a comparison for a select number of cases (Encrenaz et al. 1998). It is evident from this figure that the best fit to the data are obtained with $q_{CH_4} = 3 \times 10^{-5}$, $K_h = 1 \times 10^4$ cm^{2}s^{-1}, or with $q_{CH_4} = 1 \times 10^{-4}$, $K_h = 5 \times 10^3$ cm^{2}s^{-1}, where K_h is the value of the eddy diffusion coefficient at the Uranus homopause, and K is assumed to vary inversely as the square root of the atmospheric number density, n, i.e. $K \propto n^{-0.5}$. For the best fit values of K_h, the homopause is located at 354 km (0.04 mb) above the 1-bar level for $K_h = 5 \times 10^3$ cm^{2}s^{-1}, and at 390 km (0.02 mb) for $K_h = 1 \times 10^4$ cm^{2}s^{-1}.

The above results on the eddy diffusion coefficient from ISO are in agreement with the Voyager results. The analysis of Voyager ultraviolet solar occultation data yielded a range of $(3 - 10) \times 10^3$ for K_h (Herbert et al. 1987; Summers and Strobel, 1989; Bishop et al. 1990; Atreya et al. 1991). The only low value from Voyager came from the modelling of the 128 nm Raman scattered emission in the subsolar region, which implied a value of 100 cm^{2}s^{-1} (Yelle et al. 1989). This result corresponds to the 0.5-100 mb region, however. If extrapolated to the above-mentioned homopause levels using the above dependence of K on n, even these reflection spectroscopy data give the same results as obtained by the Voyager occultation technique. The Voyager measurements were done 10 years prior to the ISO observations. The south pole of Uranus was pointing to the Sun at the time of the Voyager observations, whereas the subsolar latitude was ~45°S when the ISO data were collected, as shown in Fig. 3. Moreover, the Voyager solar occultation data from which the vertical mixing was derived corresponded to the equatorial latitudes, whereas the ISO results are globally averaged. It seems puzzling therefore that these two sets of data
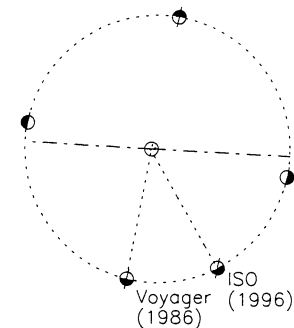
under two vastly different observation geometries and solar insolation conditions should give nearly identical results on the vertical mixing in the Uranus upper atmosphere. A plausible explanation may be related to the fact that the internal heat on this planet is very small, not exceeding 14% of the absorbed solar flux (Conrath et al. 1991). The sluggish vertical mixing in the Uranus atmosphere appears to be due to the low energy balance of this planet. Since the internal heat is expected to be fairly uniform over the planet and will not vary over the short time span of ten years between the Voyager and ISO observations, it is expected that the dynamical behaviour, particularly the vertical mixing will also be uniform and essentially time invariant, at least on a short time scale, as is implied by the ISO and Voyager datasets. It would be instructive to carry out similar observations in the future, e.g. with SIRTF, to see if the vertical mixing in the Uranus atmosphere continues to behave in the same way as in the previous decade.

2. ISO DETECTION OF CH_3 ON SATURN: ATMOSPHERIC VERTICAL MIXING, AND CHEMICAL KINETICS

The first ever detection of the methyl radicals (CH_3) in the outer solar system was made in Saturn's atmosphere by ISO/SWS in December 1997, at 16.5 μm. in the ν_2 band Q-branch (Bézard et al. 1998a). The resulting CH_3 column abundance at the methane homopause — $(1.5 - 7.5) \times 10^{13}$ cm^{-2} — is about a factor of 10 lower than the predictions of methane photochemical models, such as the one we used to interpret the ISO Uranus data discussed above. Most recent models which include oxygen chemistry as well give an even greater abundance for CH_3 (Ollivier et al. 1998). (Note that the discrepancy between the CH_3 data and models for Neptune is relatively modest (Bézard et al. 1998b), which seems consistent with the much greater temperature (≥ 180 K) in the relevant range on this planet than in Saturn's atmosphere, as will be apparent below.) The photochemical distributions of CH_3 and the other products of methane photochemistry in Saturn's atmosphere based on our model are shown in Fig. 4.
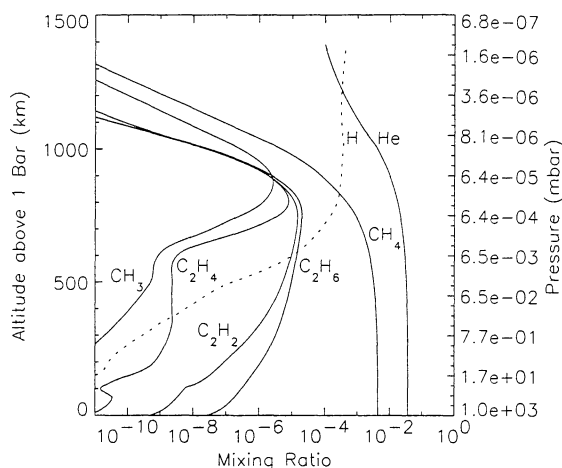
Figure 4. Hydrocarbon distribution model of Saturn.

The discrepancy between the ISO measured abundance of CH_3 on Saturn and the model results is disconcerting, as the methyl radicals play a crucial role in the photochemistry of the outer solar system. It has been suggested that either by reducing the atmospheric vertical mixing or making the loss of CH_3 more efficient in the photochemical models could bring the models closer to the data (Bézard et al. 1998a). One possibility is that the models employ too large a value for the eddy diffusion coefficient, K. All models use the values measured by Voyager. A lower value of K, on the other hand, will result in the lowering of the homopause, hence of the methane photochemical regime. Subsequently, the 3-body loss of the CH_3 molecules by the reaction,

$$CH_3 + CH_3 + M \rightarrow C_2H_6 + M \qquad (1)$$
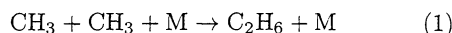
where M is the background gas (primarily H_2), will take place in a denser part of the atmosphere, thus hastening its loss rate, thereby reducing the CH_3 abundance. Data from three independent observation techniques have been analyzed by three independent groups, with all yielding a value of approximately 10^8 cm^{2}s^{-1} for the eddy diffusion coefficient, as shown in Table 1.

The value of K_h required to reduce the model CH_3 to the abundance measured by ISO is at least a factor of 100 lower than the Voyager derived value (Bézard et al. 1998; Atreya et al. 1998). We do not find any reason to believe that such a reduction in K_h could have taken place in the sixteen years that elapsed between the Voyager and the ISO observations. Moreover, the recent analysis of the CH_4 fluorescence data from ISO confirms the Voyager result on K_h (Drossart et al. 1998). It is true that the ISO CH_3 data correspond to globally averaged conditions as opposed to the nearly equatorial results from Voyager. However, the globally averaged values of the atmospheric vertical mixing coefficient are not expected to be lower than the Voyager derived equatorial values, because of the energy input from the magnetospheric charged particles at high latitudes.

We believe instead that the choice of the rate constant, k, for reaction (1) in the models is incorrect, leading to an overestimate of the CH_3 abundance in Saturn's atmosphere (Atreya et al. 1998). Laboratory measurements have been done at room temperatures and higher (T≥296 K). All recent photochemical models employ a value of k which is extrapolated to lower temperatures using expressions fitted to data at high temperatures. The most relevant temperature for the loss region of CH_3 on Saturn is approximately 140 K. Even if one were to believe that such extrapolation from 296 K to 140 K is correct, an examination of the extrapolated data from two recent lab measurements shows wide discrepancies in k (Fig.
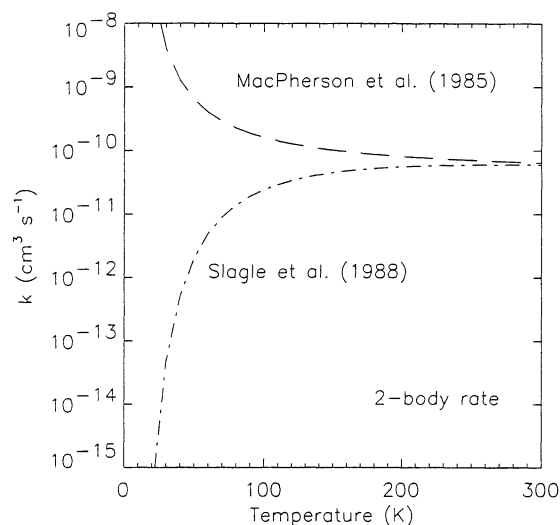

Figure 5. Rate constants for $CH_3 + CH_3 \rightarrow C_2H_6$ reaction (2-body)

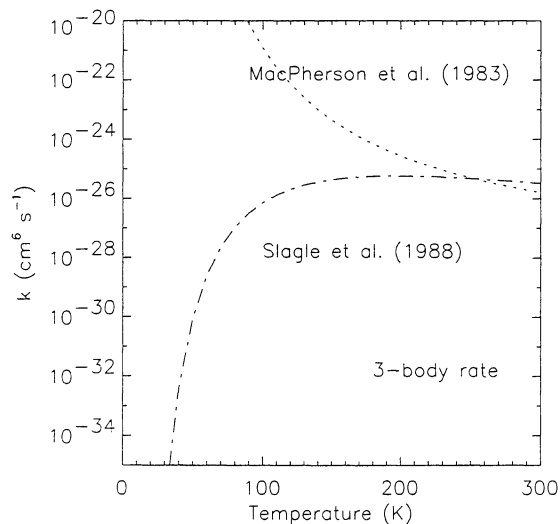*Figure 6. Rate constants for $CH_3 + CH_3 \rightarrow C_2H_6$ reaction (3-body)*

Table 1. Eddy Diffusion Coefficient, K_h, at Saturn's Homopause (in $cm^2 s^{-1}$)

Measurement	K_h	Reference
Solar/Stellar Occultations, and H Ly-α	$1.7(+4.3, -1.0) \times 10^8$	(Atreya 1982)
He 584 Å, and Solar/Stellar Occultations	$0.8(+0.4, -0.4) \times 10^8$	(Sandel et al. 1982)
He 584 Å (reanalysis)	$\geq 10^8$	(Parkinson et al. 1998)[†]

[†]considering the uncertainties in the various parameters of their model, the authors
of the last entry regard their results as being in agreement with the previous two

5: 2-body rate, and Fig. 6: 3-body rate). At 140 K, the values of k differ by a factor of 3 for 2-body rates, and a factor of 300 for 3-body rates! And, it is the 3-body rate which is most relevant for the CH_3 loss mechanism in the atmosphere. All models use the Slagle et al. (1988) data. It is clear that if the higher, MacPherson et al. (1983) data were used, the models will yield a drastically lower abundance of CH_3, in fact too low in comparison with the ISO result. It is remarkable too that the low temperature extrapolations of the two data sets diverge from each other. Note also that these data were collected using argon as the bath gas, whereas H_2 is the relevant bath gas in the context of Saturn. In view of these uncertainties, it is clear that a larger value of k than used in the models is entirely feasible. Choice of an appropriate value of k, while still using the Voyager values of eddy mixing, can give a model CH_3 abundance that matches the ISO result. Finally, yet another mechanism of the loss of CH_3, i.e. its reaction with H atoms, including possibly "hot" H-atoms, must be reevaluated under appropriate lab conditions. At the same time, modelers should be cautious that parametric studies by tweaking the CH_3 rates are robust enough to fit the other measured hydrocarbon species as well in a self-consistent manner.

3. CONCLUSIONS

The ISO observations of acetylene in the atmosphere of Uranus and the methyl radicals in the Saturn atmosphere have reaffirmed the strengths of vertical mixing measured by Voyager a decade or more ago. It is indicated that the Uranus upper atmosphere is quite placid, uniform and time invariant from point of view of its dynamics. The detection of methyl radicals on Saturn has revealed weaknesses in photochemical models. As we embark on ambitious missions such as Cassini-Huygens, it is imperative that appropriate laboratory data be collected at the temperatures, pressures, and other conditions such as the bath gas relevant to the environments of the planets and satellites being observed.

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