ISO OBSERVATIONS OF C$_2$H$_2$ ON URANUS AND CH$_4$ 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$_2$H$_2$). Interpretation of the C$_2$H$_2$ density profile with photochemical models leads to a value of (5 – 10) x 10$^{13}$ 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) x 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$_2$H$_2$ ON URANUS:
ATMOSPHERIC VERTICAL MIXING

The Short Wavelength Spectrometer on the Infrared Space Observatory (ISO/SWS) detected unambiguously in 1996 the ν$_6$ band signature of acetylene (C$_2$H$_2$) centered at 13.7 μm. (Encrenaz et al. 1998). C$_2$H$_2$ 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 Mordant et al. (1993). Combining these data with earlier laboratory results leads to a quantum efficiency of 0.41 for CH$_3$, 0.1 for CH, 0.28

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for $^1$CH$_2$ and 0.21 for $^3$CH$_2$ (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$_2$H$_2$, 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 $\sim 45^\circ$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 $\mu$m in the $v_3$ 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 $(\geq 180$ 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.
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 $\text{CH}_3$ abundance in Saturn’s atmosphere (Atreya et al. 1998). Laboratory measurements have been done at room temperatures and higher ($T \geq 296$ 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 $\text{CH}_3$ 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. 5).

$$\text{CH}_3 + \text{CH}_3 + \text{M} \rightarrow \text{C}_2\text{H}_6 + \text{M}$$

(1)

where M is the background gas (primarily $\text{H}_2$), will take place in a denser part of the atmosphere, thus hastening its loss rate, thereby reducing the $\text{CH}_3$ abundance. Data from three independent observation techniques have been analyzed by three independent groups, with all yielding a value of approximately $10^6$ cm$^3$s$^{-1}$ for the eddy diffusion coefficient, as shown in Table 1.

The value of $K_a$ required to reduce the model $\text{CH}_3$ 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 $K_a$ could have taken place in the sixteen years that elapsed between the Voyager and the ISO observations. Moreover, the recent analysis of the $\text{CH}_4$ fluorescence data from ISO confirms the Voyager result on $K_a$ (Drossart et al. 1998). It is true that the ISO $\text{CH}_3$ 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.
Table 1. Eddy Diffusion Coefficient, $K_h$, at Saturn’s Homopause (in cm$^2$s$^{-1}$)

<table>
<thead>
<tr>
<th>Measurement</th>
<th>$K_h$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solar/Stellar Occultations, and H Ly-$\alpha$</td>
<td>$1.7(+4.3, -1.0) \times 10^8$</td>
<td>(Atreya 1982)</td>
</tr>
<tr>
<td>He 584 Å, and Solar/Stellar Occultations</td>
<td>$0.8(+0.4, -0.4) \times 10^8$</td>
<td>(Sandel et al. 1992)</td>
</tr>
<tr>
<td>He 584 Å (reanalysis)</td>
<td>$\geq 10^8$</td>
<td>(Parkinson et al. 1998)$^1$</td>
</tr>
</tbody>
</table>

$^1$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, models 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 confirmed 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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