AN UPDATED HYDROCARBON PHOTOCHEMICAL MODEL FOR THE JOVIAN ATMOSPHERE FROM THE TROPOSPHERE THROUGH THE HOMOPAUSE: A PRELUDE TO GALILEO

M. Allen
Jet Propulsion Laboratory, California Institute of Technology

G. R. Gladstone and Y. L. Yung
California Institute of Technology

A photochemical model for the atmosphere of Jupiter, including 1-D vertical eddy diffusive transport, has been developed. It extends from the upper troposphere (pressure <5 bar) through the homopause. The hydrocarbon chemistry involves species containing up to four carbon atoms (and polyynes through C_8H_2). The calculations show that a large fraction of photochemical carbon may be contained in molecules with more than two carbon atoms. At the tropopause ($\approx$ 164 mb), C_2H_6 is the major photochemical species and C_2H_2, C_3H_8, and C_4H_{10} are of comparable abundance and down from C_2H_6 by a factor of ten. These species may be detectable with the mass spectrometer of the Galileo Probe. The vertical distributions of the photochemical species are sensitive to the magnitude of eddy diffusive mixing in the troposphere and stratosphere and the details of the interface region.

I presume that our paper was placed in this session on future spaceflight opportunities because of the last four words of our title. It is not necessarily inappropriate because I wish at the end to throw out a challenge to the Galileo Probe to detect something predicted by our models to exist but which has not yet been detected. You may have noticed that in his review Darrell Strobel did not emphasize the hydrocarbon chemistry modeling, essentially because nothing much has occurred in the past few years. Most of the action has been centered on phosphorus. There has been a fair amount of new observational information coming from Voyager, and with an eye towards Galileo we've decided to reopen the analysis of hydrocarbon modeling of Jupiter. Some of you may have heard me talk about some of the results from our work at the DPS Meeting in Hawaii. I'd like to talk about other new results this morning.

As for the basic details of the model, we now run the model from the 5 bar level in the troposphere up through the homopause. The Voyager data are used to define the temperature-pressure profile. We have expanded the model to include more complex hydrocarbon species than you find in other published hydrocarbon models for Jupiter. Much of this is a result of our work for Titan where, because of the complex molecules that were seen, it was necessary for us to make a major effort to expand the reaction set. Now we are going back to see if the same basic reactions will help us understand Jupiter. One hopes that the chemistry is the same, independent of where you are in the solar system.

Since this is still a classic one-dimensional model, the transport is vertical mixing through eddy diffusion. We employ a stratospheric profile for the eddy diffusivity that Randy Gladstone used in his thesis; it is similar to what other people have used in the past. Then there is the question of how fast is the mixing in the troposphere? Darrell Strobel mentioned values of the eddy diffusivity for the upper troposphere on the order of 10^4 cm^2s^{-1} based on work with Marty Tomasko, but dynamical arguments suggest that at some level in the troposphere the mixing may imply a coefficient as large as 10^8 cm^2s^{-1}. The modeling that I will describe assumes a constant value of 10^4 cm^2s^{-1} throughout the troposphere, but I'll surmise about what would be the effects if you had more rapid mixing. So the basic eddy diffusion profile we use has fast mixing (10^7 cm^2s^{-1}) up high as inferred by the Voyager UVS observations, decreases to a more stagnant layer ($<10^3$ cm^2s^{-1}) in the stratosphere, and then jumps up to faster mixing in the troposphere. This kind of profile is similar to what is used in Earth modeling, with a sharp discontinuity occurring at the tropopause.

We use diurnally averaged radiation field calculations, which should be valid for most species on Jupiter given their lifetimes. In addition to the basic reactions involving C_1 and C_2, we have a reaction set for a host of C_3 and C_4 compounds. Rather than describe the many pathways, I want to emphasize the fact that you get these more complex species through 3-body recombination between C_1 and C_2 radicals. So combination of C_2H_3 and C_2H_5 produces C_4H_8, and the C_4H_{10} comes from C_2H_5. With recombination between C_1 and C_2H_2, one gets allene and methyl-acetylene. There are tentative detections reported for some of these species, but many are undetected. I should note that our reaction set at the C_4 level is not thoroughly complete, so that the results we obtain for butane may be an upper limit. Another point that I should make is that some of these reactions were previously discussed by Jack McConnell at a DPS meeting some years ago.

Among the basic results of our model is the fact that we have allene, methyl-acetylene, and ethene, which are species that have been reportedly detected very recently. However, I particularly want to point out that in the lower stratosphere, we find abundances of propane and butane that are almost equal to the abundance of acetylene.

In fact, when you count up the number of carbon atoms, you find that there may be as much "photochemical" carbon contained in these species as is contained in acetylene. It is very interesting that none of these species have been reported so far. I would like to suggest a reason for that and relate it to the question of potential Galileo measurements.

The molecules with multiple bonds such as acetylene, methyl-acetylene, and ethene have spectroscopic characteristics that are significantly different from molecules that are fully saturated and hence have no multiple bonds (e.g., ethane, propane, and butane). The saturated molecules tend to have very smooth absorption that cuts off very sharply between 1600 and 1700 Å, whereas those with multiple bonds have a tendency to absorb at much longer wavelengths. This situation leads to problems in trying to detect the more saturated species because of the rapid decrease in solar illumination at shorter wavelengths in the ultraviolet. It makes things very difficult for

the IUE. The lack of structure also makes the identification of the signature for a particular species problematic. At the same time, the molecules with multiple bonds have fairly intense bands in the infrared, while those of the saturated molecules are relatively weak (down by a factor of 10 to 100). In fact, the only reason that one might see ethane is that it is so abundant relative to acetylene. When you start looking for saturated species which have abundances on the order of that for acetylene, then you will have trouble because you are fighting the spectroscopy.

Now I would like to pose the challenge for the mass spectrometer on the Galileo Probe, namely, the detection of one or more of these trace species. Because of the predicted decrease in mixing ratio towards the troposphere, a crucial issue in addition to its sensitivity will be the altitude at which the mass spectrometer begins to obtain data. It is my understanding that the mass spectrometer turns on at the 100 mb level and has a sensitivity of one part in 10^9. Because we have added a rapidly mixed troposphere instead of cutting off our model at the tropopause as most previously published models, the vertical mixing propagates up into the stratosphere. Even though the species in the lower stratosphere tend to be long-lived, there is sort of a "vacuum cleaner" effect on the troposphere, leading to a decrease in the mixing ratio profile starting somewhat above the tropopause and extending down into the troposphere. This is in contrast to the kinds of modeling that are done for remote sensing analyses in which constant vertical mixing ratios are assumed throughout the stratosphere. If the mass spectrometer has sufficient sensitivity starting at 100 mb, one might even see the decrease in the profile above the tropopause predicted by our more realistic modeling of the transport in the one-dimensional limit. If you increase the mixing in the troposphere by taking an eddy diffusivity of 10^8 cm^2s^{-1} instead of 10^4 cm^2s^{-1}, then the tropospheric profiles will drop even further, and there will be even sharper cut-offs in the stratosphere. In that case, we may miss completely any potential window for detection of the trace species by the mass spectrometer. Whether or not we see these trace species may therefore give us some information about the transport in the atmosphere.

DR. LUNINE: Mark, a lot of the photochemistry that you've talked about is also applicable to the other outer planets and also to Titan. There are some uncertainties I know, that have plagued these models for a while. Which of these uncertainties will be at least constrained, or possibly eliminated by the ability to measure vertical profiles through one of these atmospheres? Or will all the uncertainties remain buried in vertical transport?

DR. ALLEN: I think that, given our ability to do remote sensing, and the observations that are just coming out now based on some Voyager and IUE data, there is a possibility that we can attempt to confirm our reaction sequence to some extent in the upper stratosphere from remote sensing. Then hopefully, if we gain more confidence from looking at species in the stratosphere, tying that in with our understanding of Titan and the visibility of propane on Titan, maybe in the end we can have some hope of then saying that the ability to detect species depends on the sensitivity threshold. So you see, the mass spectrometer may actually succeed and we can then back out some statement about transport and mixing on Jupiter.

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DR. NIEMANN: I suppose you would like to know what the probe mass spectrometer can do to verify your predictions. This is quite a challenge to the mass spectrometer. The present mission design does not cover the altitude or pressure range where you predict the relatively high and measurable hydrocarbon concentrations. However, we have a chemical enrichment cell in the instrument, and our laboratory tests have shown that we may get a factor of 200 or more enrichment depending on the species. This will be one sample averaged over an altitude of several kilometers. Mass spectrometers have a problem, particularly when they are operated in hydrogen, of generating their own hydrocarbons up to the C_3 level, which effectively lowers the detection threshold for these species. So in the direct measurement mode, without the enrichment cells, we will be below the detection threshold of the instrument, but with the enrichment cells we have a chance to see some of the species. However, we will not have any altitude resolution.

DR. ORTON: The Stony Brook group and I are reporting a detection of propane over the infrared bright region in the northern hemisphere in the Voyager IRIS data.

DR. ALLEN: I was in fact talking with Ken and Richard Wagener about those results and interestingly enough, the fact that you see these species in the North Polar region may not be a function of unique chemistry there, but may be an observability factor. When you are looking from Ken's point of view, the contribution level of the atmosphere that you're seeing near the pole is much higher than it is when you're looking towards the equatorial regions. If you remember, our profiles show a maximum in the stratosphere rather than a constant mixing ratio. That means that if you're looking up at <10 mb, you have sensitivity for these various species that I'm talking about. When you're looking more at the 20 mb level corresponding to observations at lower latitudes, you have less sensitivity. So it may turn out that in fact there is nothing funny in the chemistry at the poles that makes propane more abundant; it may be which level in the atmosphere you're observing.