PHOSPHINE AND AMMONIA PHOTOCHEMISTRY IN JUPITER'S TROPOSPHERE. C. Visscher[1], A. D. Sperier[2], J. I. Moses[1], and T.C. Keane[3]. [1]Lunar and Planetary Institute, USRA, 3600 Bay Area Blvd., Houston, TX 77058-1113 [2]Baylor University, Waco, TX 76798, [3]Department of Chemistry and Physics, The Sage Colleges, Troy, NY 12180, (visscher@lpi.usra.edu, moses@lpi.usra.edu)

Introduction: The last comprehensive photochemical model for Jupiter's troposphere was presented by Edgington et al. [1,2], based upon the work of Atreya et al. [3] and Kaye and Strobel [4-6]. Since these early studies, numerous laboratory experiments have led to an improvement in our understanding of PH_3, NH_3-PH_3, and NH_3-C_2H_2 photochemistry [7-13]. Furthermore, recent *Galileo*, *Cassini*, and Earth-based observations have better defined the abundance of key atmospheric constituents as a function of altitude and latitude in Jupiter's troposphere. These new results provide an opportunity to test and improve theoretical models of Jovian atmospheric chemistry. We have therefore developed a photochemical model for Jupiter's troposphere considering the updated experimental and observational constraints.

Using the Caltech/JPL KINETICS code [14] for our photochemical models, our basic approach is twofold. The validity of our selected chemical reaction list is first tested by simulating the laboratory experiments of PH_3, NH_3-PH_3, and NH_3-C_2H_2 photolysis with photochemical "box" models. This reaction list is then used to produce a photochemical model for the Jovian troposphere.

Simulations of Laboratory Experiments: A box model involving 30 species and 220 reactions is used to simulate the photolysis experiments of Ferris et al. [5,6], in which PH_3 or NH_3/PH_3 mixtures were UV-irradiated in photochemical cells. Wherever possible, reaction rate coefficients used in our model are obtained from experimental and literature data or calculated from reverse reaction rates. For important reactions with poorly known rate coefficients, estimated reaction rates are adjusted until good agreement was achieved between our model and experimental results.

One outcome is shown in Figure 1, which compares abundances in a photochemical box model to the laboratory results of Ferris et al. [8] for a 50/50 NH_3/PH_3 mixture at 298 K and 11 torr total pressure. As in the experiments, the dominant products in our box model were H_2, diphosphine (P_2H_4), and red phosphorus (P_x). The net conversion of phosphine into red phosphorus in the model follows the pathway $PH_3 \rightarrow PH_2 \rightarrow P_2H_4 \rightarrow P_2H_3 \rightarrow P_2H_2 \rightarrow P_2H \rightarrow P_2 \rightarrow P_x$. This pathway generally occurs in either the absence or presence of NH_3. In mixtures containing a greater proportion of ammonia, amino-phosphine (NH_2PH_2) also becomes an important product and chemical reactions involving the amino radical (NH_2) play a larger role. We note that this is the first photochemical model to include P_2H as an intermediate species in PH_3 photolysis. The equivalent N_2H_x species are believed to be important in the combustion chemistry of nitrogen compounds [15].

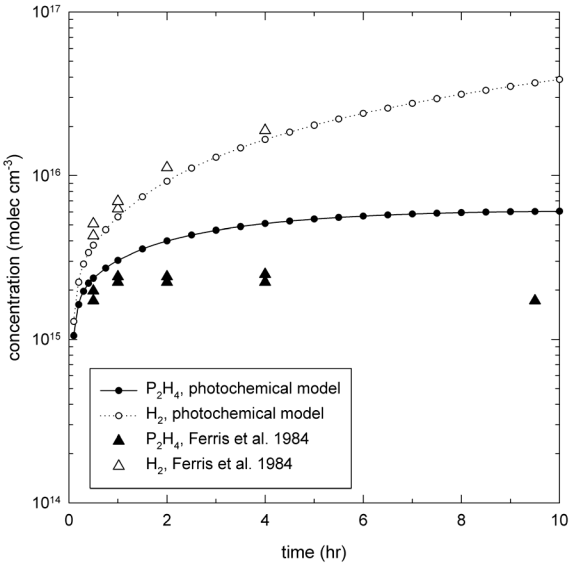

Figure 1: Comparison of H_2 and P_2H_4 production in a photochemical "box" model to the laboratory measurements of Ferris et al. [8] for a photochemical cell containing a 50/50 mixture of NH_3/PH_3 at 298 K and 11 torr (14.7 mbar) total pressure. Diphosphine production drops more rapidly in the laboratory data because red phosphorus began to coat the cell window in the experiments, reducing the available UV flux.

Preliminary Results for Jovian Tropospheric Photochemistry: The chemical reaction list adopted from experimental simulations is used to produce a one-dimensional (in altitude) photochemical model for Jupiter's troposphere. The Jupiter model includes 180 species and over 1300 reactions. Atmospheric transport in the model occurs by eddy and molecular diffusion. Eddy diffusion, which is a free parameter in the model, is adjusted to test its effect on the vertical profile of key atmospheric constituents (such as PH_3 and NH_3). The abundances of the major parent species CH_4, PH_3, and NH_3 (the dominant C-, P-, and N-bearing gases, respectively) are fixed at the lower boundary (~7 bar) using values from spectroscopic and *Galileo* probe observations.

Preliminary model results are given in Figure 2, which shows the major products of PH_3 and NH_3 photochemistry in Jupiter's troposphere. The abundance of acetylene (C_2H_2) is also shown because it has been suggested as an important hydrocarbon species for coupling with PH_3 or NH_3 photochemistry [4-6,9,10].

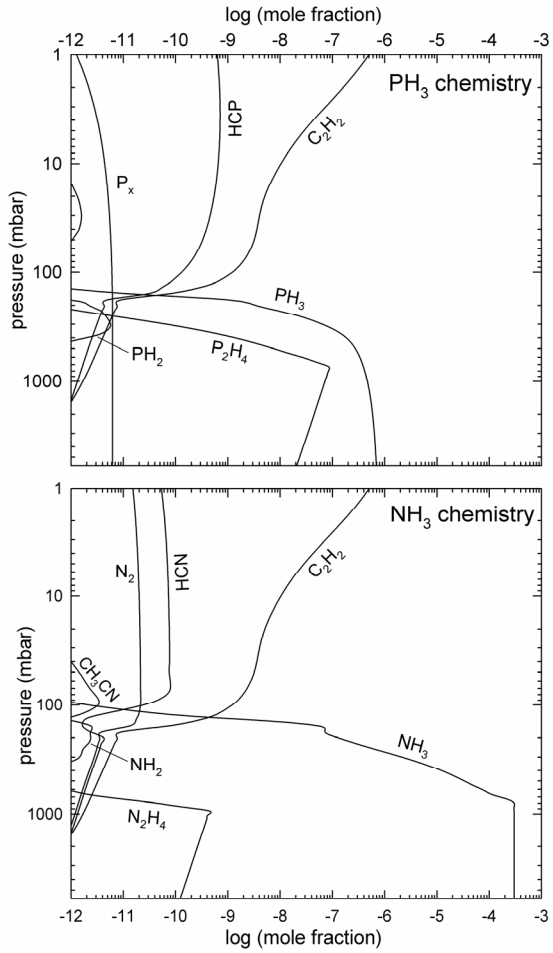

Figure 2. Model results for photochemistry in Jupiter's troposphere, showing the major products of PH_3 (top) and NH_3 (bottom) photolysis.

Conclusions: The dominant products of NH_3 and PH_3 photolysis are diphosphine (P_2H_4), hydrazine (N_2H_4), red phosphorus (P_x), and amino-phosphine (NH_2PH_2), all of which are expected to condense in Jupiter's upper troposphere. Because of its relatively high production rate in both the laboratory experiments and the photochemical models, P_2H_4 is expected to be an important, albeit underappreciated, aerosol component on Jupiter. Furthermore, several of the products of PH_3, NH_3 and NH_3-C_2H_2 photochemistry have been identified as potential chromophore candidates in Jupiter's atmosphere [16].

The tropospheric abundance of PH_3 as a function of altitude is sensitive to both the aerosol opacity and the eddy diffusion coefficient, especially in the 100-1000 mbar region. In contrast, the NH_3 abundance is mostly independent of variations in the eddy diffusion coefficient because ammonia condenses near the 800 mbar region. The modeled vertical profile of NH_3 follows its saturation vapor pressure curve between 200-800 mbar.

The main products of coupled PH_3-C_2H_2 and NH_3-C_2H_2 photochemistry are HCP and HCN, respectively. Acetylene is abundant in Jupiter's stratosphere, but rapidly decreases with depth [17]. The low abundance of C_2H_2 in the troposphere prevents coupled photochemistry from readily occurring. Therefore, relatively small amounts of HCN are produced, well within the observational upper limits of ~ 1 ppb [18]. For the same reason, even smaller amounts other compounds which have been produced in the laboratory, such as nitriles and hydrazones [9,10], are expected to be produced in the Jovian troposphere. Coupled PH_3-C_2H_2 and NH_3-C_2H_2 photochemistry is therefore not expected to be important on Jupiter.

References: [1] Edgington S. G. et al. (1998) *Icarus, 133,* 192-209. [2] Edgington S. G. et al. (1999) *Icarus, 142,* 342-356. [3] Atreya S. K. et al. (1977) *Icarus, 31,* 348-355. [4] Kaye J. A. and Strobel J. F (1983) *Icarus, 54,* 417-433. [5] Kaye J. A. and Strobel J. F (1983) *Icarus, 55,* 399-419. [6] Kaye J. A. and Strobel J. F (1984) *Icarus, 59,* 314-355. [7] Ferris J. P. and Benson R. (1981) *J. Am. Chem. Soc., 103*, 1922-1927. [8] Ferris J. P. et al. (1984) *J. Am. Chem. Soc., 106*, 318-324. [9] Ferris J. P. and Ishikawa Y. (1988) *J. Am. Chem. Soc., 110,* 4306-4312. [10] Keane T. C. et al. (1996) *Icarus, 122,* 205-207. [11] Guillemin J.-C. et al. (1995) *Adv. Space Res., 16,* (2)85-(2)92. [12] Guillemin J.-C. et al. (1997) *Adv. Space Res., 19,* 1093-1102. [13] Guillemin J.-C. et al. (2001) *Adv. Space Res., 27,* 245-253. [14] Allen M. et al. (1981) *JGR*, 86, 3617-3627. [15] Dean A. M. and Bozzelli J. W. (2000) in Gas-Phase Combustion Chemistry (edited by W. C. Gardiner, Jr.), 125-341. [16] West R. A. et al. (1986) Icarus, 65, 161-217. [17] Moses J. I. et al (2004) in *Jupiter: The Planet, Satellites, and Magnetosphere* (edited by F. Bagenal, T. Dowling, and W. McKinnon), 129-157. [18] Davis G. R. et al. (1997) *Icarus, 130,* 387-403.

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