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Modeling the disequilibrium species for Jupiter and Saturn: Implications for Juno and Saturn entry probe

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ABSTRACT

Disequilibrium species have been used previously to probe the deep water abundances and the eddy diffusion coefficient for giant planets. In this paper, we present a diffusion-kinetics code that predicts the abundances of disequilibrium species in the tropospheres of Jupiter and Saturn with updated thermodynamic and kinetic data. The dependence on the deep water abundance and the eddy diffusion coefficient is investigated. We quantified the disagreements in CO kinetics that comes from using different reaction networks and identified C_2H_6 as a useful tracer for the eddy diffusion coefficient. We first apply an H/P/O reaction network to Jupiter and Saturn's atmospheres and suggest a new PH_3 destruction pathway. New chemical pathways for SiH_4 and GeH_4 destruction are also suggested, and another AsH_3 destruction pathway is investigated thanks to new thermodynamic and kinetic data. These new models should enhance the interpretation of the measurement of disequilibrium species by JIRAM on board Juno and allow disentangling between methods for constraining the Saturn's deep water abundance with the Saturn entry probes envisaged by NASA or ESA.

1. Introduction

Disequilibrium species in the atmosphere of Jupiter and Saturn can be used to constrain the deep water abundance and the deep eddy diffusion coefficient in the atmospheres of Jupiter and Saturn (e.g., Prinn and Barshay, 1977; Fegley and Lodders, 1994). Various disequilibrium species such as CO, PH_3, GeH_4, and AsH_3 have been detected on Jupiter and Saturn with abundances orders of magnitude higher than their respective chemical equilibrium abundances at the pressure level where they are observable (e.g., Beer, 1975; Noll et al., 1986; Ridgway et al., 1976; Larson et al., 1980; Fink et al., 1978; Noll et al., 1988; Bézard et al., 1989; Noll et al., 1989). These species at a few bars are transported upward by vertical mixing from the deep atmosphere where they are more abundant, therefore, they contain the information of the atmosphere down to a few hundred bars. In this paper, we model the vertical profiles of disequilibrium species with updated thermodynamic and kinetic data. The dependence on the water abundance and the eddy diffusion coefficient is investigated.

Our study is timely for the following reasons. The JIRAM instrument on board the Juno spacecraft will be able to measure the disequilibrium species CO, PH_3, GeH_4, and AsH_3 down to a few bars when it will arrive at Jupiter in 2016 (Grassi et al., 2010). The microwave radiometer onboard Juno will also be able to measure the deep water abundance (Janssen et al., 2005). With the abundances of disequilibrium species and water, constraints should be made on the deep eddy diffusion coefficient. A Saturn probe proposal has been submitted to the ESA 2015 call for medium class mission (Mousis et al., 2015) and a similar concept is under study for a submission to the NASA 2016 New Frontier call(Atkinson et al., 2012). Current entry probes are designed to go down to 10–20 bar and can make in-situ measurements of the atmosphere composition via mass spectrometry (Wong et al., 2004). However, it is unlikely that such probes will be able to descend below the water cloud deck and measure the deep water abundance. A study with the updated kinetic data is then necessary for evaluating whether deep water abundance can be effectively constrained by disequilibrium species.

We use the diffusion-kinetic model developed in Wang et al. (2015). A C/N/O/H reaction network is employed to predict the abundances of various carbon bearing species. The reaction networks for P/H/O and Si/H/O species are applied for the first time to study planetary atmospheres in this paper. New chemical pathways for PH_3 and GeH_4 destructions are then proposed. New compilations of thermochemical data, especially for P, Ge, and As, are used in our model.

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Table 1
Observed mixing ratios of some disequilibrium species.

	Jupiter		Saturn	
	q	References	q	References
CO	$1.0 \pm 0.2 \times 10^{-9}$	Bézard et al. (2002)	$< 1.0 \times 10^{-9}$	Cavalié et al. (2009)
PH_3	$8 \pm 1 \times 10^{-7}$	Irwin et al. (1998)	$4 \pm 1 \times 10^{-6}$	Fletcher et al. (2011)
SiH_4	$< 2.5 \times 10^{-9}$	Treffers et al. (1978)	$< 2 \times 10^{-10}$	Noll and Larson (1991)
GeH_4	$7 \pm 2 \times 10^{-10}$	Bjoraker et al. (1986)	$4 \pm 2 \times 10^{-10}$	Noll et al. (1988)
AsH_3	$2.2 \pm 1.1 \times 10^{-10}$	Noll et al. (1990)	$3 \pm 1 \times 10^{-9}$	Noll and Larson (1991)

The paper is organized as follows. In Section 2, we introduce the current status of the measurement of disequilibrium species. In Section 3, we describe our models for the chemistry and transport of disequilibrium species. In Section 4, we present our results. In Section 5, we discuss the implications for Juno and a Saturn entry probe. The conclusions are summarized in Section 6.

2. Measurements of disequilibrium species: Current status

The tropospheric abundances of CO, PH_3, SiH_4, GeH_4 and AsH_3 are primarily measured in the 5μm window for Jupiter and Saturn. Apart from a 1 ppb tropospheric component (e.g., Larson et al., 1978; Bjoraker et al., 1986), CO also has a stratospheric component (e.g., Bézard et al., 2002). The tropospheric CO is supplied by vertical convective mixing from deep levels where CO prevails (Prinn and Barshay, 1977), while the stratospheric CO can be supplied by micrometeoroids (Prather et al., 1978), infalling materials from icy satellites (Strobel, 1979), or shock chemistry from infalling kilometer to subkilometer-sized comets (Bézard et al., 2002; Lellouch et al., 1995). At Jupiter and Saturn, comets are more probable than other sources (Bézard et al., 2002; Cavalié et al., 2010). The tropospheric CO contains information on the deep atmosphere, and thus can be used to probe the deep water abundance and the deep eddy diffusion coefficient. The retrieval of Saturn's tropospheric CO has not been successful due to its very low mixing ratios (Cavalié et al., 2009). Tropospheric PH_3 was measured in the 5μm window for Jupiter with a mixing ratio of $(6 \sim 9) \times 10^{-7}$ (e.g., Kunde et al., 1982; Bjoraker et al., 1986; Encrenaz et al., 1996; Irwin et al., 1998), and for Saturn with a mixing ratio of $(3 \sim 5) \times 10^{-6}$ (e.g., Noll and Larson, 1991; de Graauw et al., 1997; Fletcher et al., 2011). The vertical profile of PH_3 was retrieved from the spectra by Cassini CIRS and VIMS (Fletcher et al., 2011; 2009a). The PH_3 abundance starts to be depleted in the upper troposphere where the pressure is about 1 bar (Fletcher et al., 2012), due to decreased eddy mixing, UV photolysis and chemical re-equilibration (Irwin et al., 2004; 1998). Tropospheric GeH_4 was identified and measured at the 5μm window (Fink et al., 1978; Noll et al., 1988) at a mixing ratio of a few times 10^{-10}. The mixing ratio of GeH_4 in the stratosphere is expected to be lower than that in the troposphere because of UV photolysis. The tropospheric AsH_3 was measured on both Jupiter and Saturn (Bézard et al., 1989; Noll et al., 1989; Noll and Larson, 1991). The mixing ratio of AsH_3 on Jupiter is about 2×10^{-10} (Noll et al., 1990), while for the Saturn, the mixing ratio is about 3×10^{-9} (Bézard et al., 1989; Noll and Larson, 1991). In Table 1, we summarize the measurements of tropospheric CO, PH_3, SiH_4, GeH_4, and AsH_3 abundances for both Jupiter and Saturn.

3. Model

3.1. Introduction to the model

We developed a code to solve the 1-D transport-kinetic equation:

$$\frac{\partial Y_i}{\partial t} = \frac{1}{\rho}\frac{\partial}{\partial z}\left(\rho K_{\text{eddy}}\frac{\partial Y_i}{\partial z}\right) + P_i - L_i, \tag{1}$$

where Y_i is the mass fraction of species i, ρ is the density of the atmosphere, z is the vertical coordinate relative to a reference point in the atmosphere (we choose the 1 bar level in the code), K_{eddy} is the vertical eddy diffusion coefficient, P_i is the chemical production rate of species i, and L_i is the chemical loss rate of species i. Both P_i and L_i have a unit of s^{-1}. The time evolution of Y_i is controlled by two physical processes: one is the chemical production and destruction of species i, and the other is its corresponding vertical transport. In the convective envelope of Jupiter and Saturn, the transport of mass is mainly by turbulent convection. Here in equation (1), the convective transport of species is approximated by diffusion transport with an coefficient K_{eddy}, which is a good approximation justified by the success of mixing length theory in explaining stellar convection (Stone, 1976). The mass fractions Y_i are initialized using their local chemical equilibrium values along the adiabat. The chemical net production rate $(P_i - L_i)$ is integrated using *Cantera*, a software toolkit developed for problems involving chemical kinetics and thermodynamics (Goodwin et al., 2015). At each time step, we call *Cantera* to do the integration and include the result in the resolution of the continuity equation. *Cantera* has been used and tested for many applications including combustion, detonation, fuel cells, batteries, etc. The integration is terminated when the mass fractions Y_i reach steady state. The code requires three kinds of input. One is the temperature pressure profile ($T - P$ profile), the second is a list of thermodynamic properties in the format of NASA polynomials (McBride et al., 1993) for each species, and a list of reactions between these species, the third is the elemental composition and the vertical eddy diffusion coefficient K_{eddy}.

The $T - P$ profiles for Jupiter and Saturn are calculated following the method described in Fegley and Prinn (1985). We choose a reference point where temperature and pressure are measured and extrapolated into the deep atmosphere assuming a dry adiabat. For Jupiter, we use $T = 427.71$ K at 22 bars as our reference point (Seiff et al., 1998). The pressure and temperature conditions lower than 22 bars are from the Galileo entry probe measurements (Seiff et al., 1998). For Saturn, we use $T = 134.8$ K at $P = 1$ bar as our reference point (Lindal et al., 1985). The heat capacity of the atmosphere used in the calculation is computed by linearly combining the heat capacities of H_2 and He, and the heat capacities of H_2 and He are from NIST-JANAF thermochemical table (Chase, 1998). The helium mixing ratio we use is 0.157 for Jupiter (Niemann et al., 1998) and 0.135 for Saturn (Conrath and Gautier, 2000). The $T - P$ profiles for Jupiter and Saturn are calculated and shown in Fig. 1. The thermodynamic and reaction data are gathered from various sources which are detailed in the following:

- *C/N/O/H reaction network*
  Our C/N/O/H reaction network used in this paper is developed based on the network from Venot et al. (2012) downloaded from the KIDA database (Wakelam et al., 2012, http://kida.obs.u-bordeaux1.fr). The network consists of 105 neutral species and 963 reactions. Among the reactions, 957 of them are reversible reactions and 6 of them are irreversible reactions. A complete list of the species can be found in Venot et al. (2012).