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### Authors

Hsu, Juno  
Prather, Michael J

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## Global long-lived chemical modes excited in a 3-D chemistry transport model: Stratospheric N<sub>2</sub>O, NO<sub>y</sub>, O<sub>3</sub> and CH<sub>4</sub> chemistry

Juno Hsu<sup>1</sup> and Michael J. Prather<sup>1</sup>

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[1] The two longest-lived, major chemical response patterns (eigenmodes) of the atmosphere, coupling N<sub>2</sub>O and CH<sub>4</sub>, are identified with the UCI chemistry-transport model using a linearized (N<sub>2</sub>O, NO<sub>y</sub>, O<sub>3</sub>, CH<sub>4</sub>, H<sub>2</sub>O)-system for stratospheric chemistry and specified tropospheric losses. As in previous 1D and 2D studies, these century-long 3D simulations show that the e-folding decay time of a N<sub>2</sub>O perturbation (mode-1: 108.4 y) caused by a pulse emission of N<sub>2</sub>O is 10-years shorter than the N<sub>2</sub>O atmospheric lifetime (118.2 y). This mode-1 can also be excited by CH<sub>4</sub> emissions due to CH<sub>4</sub>-O<sub>3</sub> stratospheric chemistry: a pulse emission of 100 Tg CH<sub>4</sub> creates a +0.1 Tg N<sub>2</sub>O perturbation in mode-1 with a 108-yr e-folding decay time, thus increasing the CH<sub>4</sub> global warming potential by 1.2%. Almost all of the 100 Tg CH<sub>4</sub> appears in mode-2 (10.1 y). **Citation:** Hsu, J., and M. J. Prather (2010), Global long-lived chemical modes excited in a 3-D chemistry transport model: Stratospheric N<sub>2</sub>O, NO<sub>y</sub>, O<sub>3</sub> and CH<sub>4</sub> chemistry, *Geophys. Res. Lett.*, 37, L07805, doi:10.1029/2009GL042243.

### 1. Introduction

[2] Chemical eigenmodes are natural solutions to a linearized system such as chemistry-transport model (CTM) simulations of atmospheric composition. In the cases identified thus far, each mode describes a spatial and seasonal pattern of many chemical species that decay in unison with a single e-folding time. The modes are linearly independent but not orthogonal, and a perturbation to one species excites all the modes [e.g., Prather, 1994].

[3] The application of this eigenvalue decomposition to atmospheric chemistry has been explained by Prather [2007], and to other systems demonstrated by Trefethen and Embree [2005]. The number of eigenmodes equals the number of independent variables in the system; however, for atmospheric composition we are concerned primarily with only a few long-lived modes since these tend to carry the largest environmental impacts. This paper examines the coupling between the major greenhouse gases N<sub>2</sub>O and CH<sub>4</sub> by characterizing for the first time the two longest-lived, major chemical eigenmodes of the atmosphere (hereafter referred to as mode-1 and mode-2) using 3-D CTM simulations. In this work, the stratospheric O<sub>3</sub> chemistry linked to N<sub>2</sub>O and CH<sub>4</sub> is simulated, and we show how CH<sub>4</sub> emissions increase N<sub>2</sub>O. In subsequent work, we will

examine how N<sub>2</sub>O emissions alter tropospheric chemistry and the abundance of CH<sub>4</sub>.

[4] Previous work, using tropospheric chemistry CTMs, identified the long-lived 3-D chemical eigenmodes and demonstrated how short-lived gases such as NO are expected to perturb the greenhouse gas CH<sub>4</sub> for decades [Derwent *et al.*, 2001; Wild *et al.*, 2001] (see also Table 2.15 of indirect GWPs by Forster *et al.* [2007]). The only work on the long-lived chemical mode involving N<sub>2</sub>O has been with a parametric 1-D model [Prather, 1998] or with 2-D models used to adjust the effective residence time of N<sub>2</sub>O for the IPCC calculation of global warming potentials [Prather *et al.*, 2001, Table 4.5]. Here we develop a linearized stratospheric chemistry for the coupled (N<sub>2</sub>O, NO<sub>y</sub>, O<sub>3</sub>, CH<sub>4</sub>, H<sub>2</sub>O)-system based on a Taylor series expansion of the full stratospheric chemistry about a climatology of trace-gas composition [e.g., McLinden *et al.*, 2001; Olsen *et al.*, 2001]. In this paper we apply simplified surface boundary conditions for NO<sub>y</sub>, O<sub>3</sub>, and a mean tropospheric loss frequency for CH<sub>4</sub>. This model is described and tested against observations in Section 2.

[5] With this efficient chemical model, we are able to run the multi-century simulations of perturbation and control runs in 3-D with the UCI CTM [Hsu and Prather, 2009] at moderately high resolution (2.8° × 2.8° × 60 layers), which are presented in Section 3. The longest-lived mode-1 has an e-folding time of 108.4 y, about 9% shorter than the N<sub>2</sub>O atmospheric lifetime of 118.2 y, consistent with the previous 1-D and 2-D results, and caused by the fact that N<sub>2</sub>O depletes O<sub>3</sub> thus hastening its own photolytic destruction. With this mode coupled to CH<sub>4</sub> via stratospheric chemistry, we are able to follow a CH<sub>4</sub> perturbation for two centuries and derive the magnitude of the induced perturbation to N<sub>2</sub>O. In section 4 we summarize these results, noting that the climate feedback in terms of greenhouse gases is positive, but small, i.e., the additional N<sub>2</sub>O from the chemical coupling of modes increases the global warming potential for CH<sub>4</sub> by only about 1%.

### 2. Linearized Stratospheric Chemistry for the {N<sub>2</sub>O, NO<sub>y</sub>, O<sub>3</sub>, CH<sub>4</sub>, H<sub>2</sub>O}-System

[6] The first identification of 3-D global atmospheric chemistry modes used multi-decadal CTM simulations that focused on the CH<sub>4</sub>-dominated eigenmode with N<sub>2</sub>O fixed [Wild and Prather, 2000]. Those calculations used a relatively complete tropospheric chemistry, on a coarse resolution CTM (8° × 10°). By including N<sub>2</sub>O and interactive stratospheric chemistry, the longest-lived mode is extended from ten to more than a hundred years, thus requiring multi-century CTM simulations. Also, with the need for more accurate stratospheric simulation, we opt for finer horizontal

<sup>1</sup>Earth System Science, University of California, Irvine, California, USA.

**Table 1.** Different Chemical Models Used in the CTM Eigenmode Calculations<sup>a</sup>

Chemical Model	Stratosphere	Troposphere
A	N <sub>2</sub> O-NO <sub>y</sub> -O <sub>3</sub> , linearized	O <sub>3</sub> , NO <sub>y</sub> sink (~30 d)
B	N <sub>2</sub> O-NO <sub>y</sub> -O <sub>3</sub> -CH <sub>4</sub> , linearized	O <sub>3</sub> , NO <sub>y</sub> sink (~30 d), CH <sub>4</sub> sink (~10 y)
C*	N <sub>2</sub> O-NO <sub>y</sub> -O <sub>3</sub> -CH <sub>4</sub> , linearized	full chemistry

<sup>a</sup>The full chemistry (C\*), multi-century simulations are ongoing.

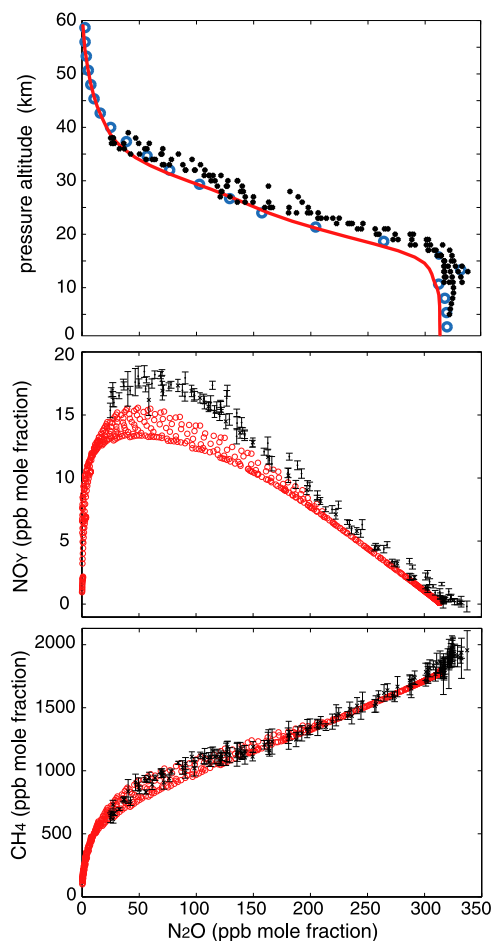
and vertical resolutions, taking the ECMWF pieced-forecast fields from Oslo U. for year 2005 at T42 ( $\sim 2.8^\circ \times 2.8^\circ$ ) L60 (60 layers) resolution [Hsu and Prather, 2009]. Thus, rather than a complete stratospheric chemistry model, we pursue a linearized ozone chemistry (Linoz) that has been remarkably successful in CTMs [e.g., McLinden et al., 2001; Hsu and Prather, 2009]. We expand upon this work by linearizing the production and loss of O<sub>3</sub>, CH<sub>4</sub>, N<sub>2</sub>O, and NO<sub>y</sub> in the stratosphere as a function of these four independent variables ( $f_j, j = 1, \dots, 4$ ) plus water vapor ( $f_5$ ) and the overhead O<sub>3</sub> column ( $c$ ) and the local temperature ( $T$ ). Water vapor is diagnosed as a dependent variable from CH<sub>4</sub> assuming a lower boundary condition of 3.65 ppm (parts per million = micromoles per mole of air) and conservation of total hydrogen as CH<sub>4</sub> is destroyed. The derivation of the linearized {N<sub>2</sub>O, NO<sub>y</sub>, O<sub>3</sub>, CH<sub>4</sub>} system as well as the tabulated climatology and partial derivative terms are archived as auxiliary material.<sup>1</sup> In the troposphere, we invoke a simple parametric loss for both O<sub>3</sub> and NO<sub>y</sub> in the lowest 4 CTM layers (surface to about 950 hPa). With a 2-day e-folding time, O<sub>3</sub> approaches 30 ppb, and NO<sub>y</sub> approaches 0.003 times the O<sub>3</sub> abundance [Murphy et al., 1993]. Tropospheric CH<sub>4</sub> loss is parameterized with an e-folding time of 4.4 y in CTM layers between 600 hPa and the surface.

[7] The UCI CTM uses one of two chemical models (A, B) for the simulations shown here, see Table 1. The third model (C\*) with full tropospheric chemistry will be reported in a separate study. Model A includes only the stratospheric N<sub>2</sub>O-NO<sub>y</sub>-O<sub>3</sub> system, leaving CH<sub>4</sub> fixed at monthly, zonal mean climatological abundances. Model A is a 3-D extension of the 1-D parametric model and thus ideal for comparison with the earlier results [Prather, 1998]. Model B uses the N<sub>2</sub>O-NO<sub>y</sub>-O<sub>3</sub>-CH<sub>4</sub> system outlined in Table 1. The CTM simulations used annually repeating meteorological data (year 2005 ECMWF T42L60 IFS cycle 29r2) and surface emissions of N<sub>2</sub>O and CH<sub>4</sub>. Annually repeating chemistry and transport is a necessary condition for the precise year-to-year e-folding of chemical perturbations. Simulations were run for several decades to achieve a near steady state.

[8] The model B control run is tested against stratospheric observations of N<sub>2</sub>O, NO<sub>y</sub> and CH<sub>4</sub> with year 2005 data from the MLS satellite instrument [Lambert et al., 2007] and recent MkIV balloon flights (Fort Sumner, NM; September 2003, 2004, 2005, and 2007 [Toon et al., 1999]) in Figure 1. The simulated average N<sub>2</sub>O vertical profile at mid-latitudes (20N–70N, September) in Figure 1 (top) (red line) matches the September 2005 MLS measurements (blue circles) but both are slightly lower than the individual profiles from the

MkIV balloon data (black crosses). The scatter plot of NO<sub>y</sub> vs N<sub>2</sub>O (Figure 1, middle) and CH<sub>4</sub> vs N<sub>2</sub>O (Figure 1, bottom) from the MkIV balloon data (black crosses with uncertainty bars) provide a good test of the linearized N<sub>2</sub>O-NO<sub>y</sub>-O<sub>3</sub>-CH<sub>4</sub> chemical model (red circles). The model matches observations except for the NO<sub>y</sub> abundances.

[9] The CTM predicts peak NO<sub>y</sub> of about 14 ppb instead of the observed 17 ppb, but the peak still occurs at about 35 km altitude where N<sub>2</sub>O ranges from 40 to 80 ppb. In a previous study of the N<sub>2</sub>O-NO<sub>y</sub> system, the UCI CTM, using a similar linearized stratospheric chemistry but different meteorological fields, was able to match the observed peak of 17 ppb [see Olsen et al., 2001, Figure 7]. That chemistry was derived from a 1999 version of the photochemical box model. In the recent update to the photochemical data for deriving Linoz tables, the solar flux data were updated, with the largest change being a 10–20% increase in the 180–220 nm flux [Hsu and Prather, 2009]. The resulting increase in photolysis rates for O<sub>2</sub> improved the simulation of O<sub>3</sub> in the stratosphere, but for NO it increased the loss rate of NO<sub>y</sub> and resulted in the discrepancy shown here.



**Figure 1.** (top) September, mid-latitude N<sub>2</sub>O vertical profiles with UCI CTM simulation (red line), Aura MLS satellite measurements (blue dots), and recent BOS-MkIV balloon measurements (black dots). (middle) N<sub>2</sub>O vs NO<sub>y</sub> scatter plot with UCI CTM simulation (red dots) and MkIV balloon (black crosses with uncertainty bars). (bottom) N<sub>2</sub>O vs CH<sub>4</sub> scatter plot with the same plotting scheme as in Figure 1 (middle).

<sup>1</sup>Auxiliary material data sets are available at <ftp://ftp.agu.org/apend/gl/2009gl042243>. Other auxiliary material files are in the HTML.

**Table 2.** Global, Annual Mean Chemical Budgets and Budget Lifetimes for the Linearized Chemistry Near Steady State<sup>a</sup>

Species	Emissions	Stratosphere		Troposphere	Lifetime
		P	L	L	
N <sub>2</sub> O (Tg-N)	13.0	0.14	13.1	0	118.2 y
NO <sub>y</sub> (Tg-N)	0	0.70	0.24	0.46	–
CH <sub>4</sub> (Tg)	500	0	32	468	9.9 y

<sup>a</sup>N<sub>2</sub>O, NO<sub>y</sub>, O<sub>3</sub>, CH<sub>4</sub>, H<sub>2</sub>O. P, production; L, loss.

[10] The chemical budgets for N<sub>2</sub>O, NO<sub>y</sub>, and CH<sub>4</sub> from the near steady-state B chemical model are given in Table 2. The budget lifetime for N<sub>2</sub>O, 118 y, is typical of current estimates [see *Forster et al.*, 2007; *Daniel et al.*, 2007]. The balance of NO<sub>y</sub> losses, with a third destroyed in the stratosphere, is similar to *Olsen et al.* [2001]. The overall CH<sub>4</sub> budget is imposed parametrically to give a total lifetime of about 10 y, but the lifetime against stratospheric loss, 155 y, is a result of the linearized stratospheric chemistry.

### 3. Identification of the Chemical Modes Coupling N<sub>2</sub>O and CH<sub>4</sub>

[11] The first two simulations were conducted with Chemistry A, one being the control run (A1), and the other one (A2) excited by an initial pulse emission of 10 Tg-N of N<sub>2</sub>O added to the surface layer (see Table 3 for a list of all model simulations). In chemistry A, the longest-lived, primary eigenmode (mode-1) is associated with decay of N<sub>2</sub>O with an e-folding time slightly less than the budget lifetime of 118 y, and the second longest mode-2, with the turnover-mixing time of the stratosphere, about 3 y. Thus in chemistry A, perturbations will revert to the slow decay of mode-1 within a couple of decades. The mode calculation (A2 minus A1) can thus identify mode-1 in about 20 years (not shown) and is summarized in Table 3. Mode amplitude is determined by extrapolating from its exponentially decaying curve back to  $t = 0$ . When extrapolated back to  $t = 0$ , mode-1 has a value of +10.2 Tg-N of N<sub>2</sub>O, paradoxically greater than the initial perturbation. Note that there is never more than 10 Tg-N at any time, even at  $t = 0$ . The initial perturbation includes short-lived modes with negative amounts of N<sub>2</sub>O and these cancel the slow, 108-year decay of mode-1. Intuitively, none of the N<sub>2</sub>O is lost in the first few years until the pulse is mixed into the middle stratosphere. The perturbations to NO<sub>y</sub> (positive) and O<sub>3</sub> (negative) are much smaller in total mass because they are primarily stratospheric, but their relative perturbations in

the middle stratosphere are similar (see later discussion, Figures 2c and 2d).

[12] Three simulations were conducted with Chemistry B, the first one being the control run (B1), the second one (B2) excited by a pulse surface emission of 10 Tg-N of N<sub>2</sub>O, same as A2, and the third one (B3) excited by a pulse surface emission of 10 Tg CH<sub>4</sub>. When CH<sub>4</sub> is included (chemistry B), the mode-2 time scale is about 10 y, set by the tropospheric loss of CH<sub>4</sub>. The mode calculation (B2 minus B1) takes only a few decades to clearly separate mode-1 from mode-2 because the CH<sub>4</sub> perturbation is very small. The time scale of mode-1 (108.4 y) and the amplitudes are very close to those found using chemistry A (It would be identical if the CH<sub>4</sub> abundances in Chemistry B were the same as the climatological values used in chemistry A). Note that mode-1 includes a small, negative amplitude of CH<sub>4</sub>. When the surface perturbation is to CH<sub>4</sub> rather than N<sub>2</sub>O, it excites mode-2 with a substantially larger amplitude than mode-1. Thus, the mode calculation (B3 minus B1) takes well over a hundred years to follow the decay of mode-2 and see mode-1 emerge in CH<sub>4</sub>. With this long perturbation sequence we can clearly identify the two modes (see Figure 2 discussion below). The 10 Tg-CH<sub>4</sub> perturbation (B3- B1) puts +10.4 Tg of CH<sub>4</sub> in mode-2 (10.1 y) and +0.006 Tg-N of N<sub>2</sub>O in mode-1 (108.4 y). Thus, the chemical coupling between N<sub>2</sub>O and CH<sub>4</sub> in the stratosphere makes emissions of CH<sub>4</sub> perturb N<sub>2</sub>O; effectively, 1000 Tg of CH<sub>4</sub> cause a concurrent perturbation that looks like an emission of 0.6 Tg-N of N<sub>2</sub>O.

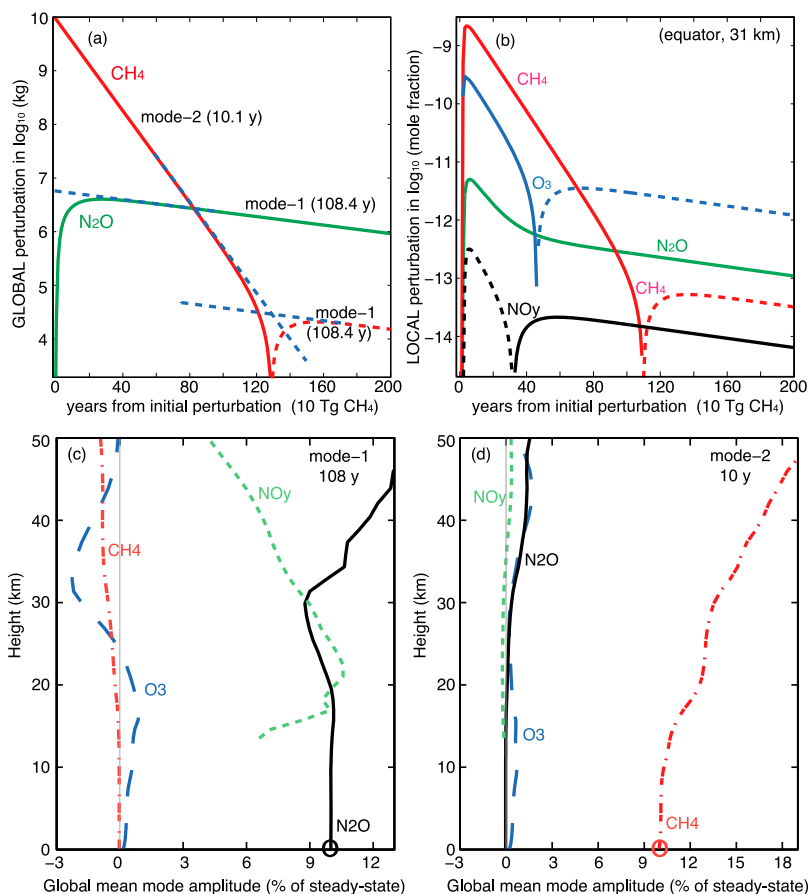
[13] In Figure 2a the total perturbed mass of both N<sub>2</sub>O and CH<sub>4</sub> are shown for the 200 years following the initial 10 Tg-CH<sub>4</sub> perturbation (B3-B1). The N<sub>2</sub>O perturbation rises from zero and after about fifty years decays according to mode-1 e-folding time (108.4 y). The CH<sub>4</sub> perturbation decays mainly with a mode-2 e-folding time (10.1 y), until after 120 years when it changes sign (dotted line) and then decays with mode-1. Perturbations to the individual abundances in the upper tropical stratosphere are shown in Figure 2b. At this location, the added CH<sub>4</sub> reaches the upper stratosphere in a few years; it reduces chlorine-catalyzed ozone depletion and thus O<sub>3</sub> increases; this in turn decreases the loss of N<sub>2</sub>O and it likewise increases. The globally integrated NO<sub>y</sub> perturbation in this early stage is negative but the vertical structure has an interesting dipole structure with negative and positive phases in the lower and upper stratosphere respectively (see Text S1 for explanations). After 50 years for ozone and 30 years for NO<sub>y</sub>, their phases reverse sign and become part of the mode-1 pattern and decay time. The initial CH<sub>4</sub> amplitude in mode-2 in the upper stratosphere is

**Table 3.** Chemical Eigenmodes and Globally Integrated Amplitudes for the A and B Chemical Models With Units in Tg-N for N<sub>2</sub>O, NO<sub>y</sub>, and Tg for the Other Species<sup>a</sup>

P-C Runs	Pulse	Mode (time)	A <sub>N<sub>2</sub>O</sub> <sup>#</sup>	A <sub>NO<sub>y</sub></sub> <sup>#</sup>	A <sub>O<sub>3</sub></sub> <sup>#</sup>	A <sub>CH<sub>4</sub></sub> <sup>#</sup>
A2-A1(30y)	10 Tg-N N <sub>2</sub> O	# 1 (108.6y)	+10.2	+0.011	-0.84	N/A
B2-B1(150 y)	10 Tg-N N <sub>2</sub> O	# 1 (108.4y)	+10.1	+0.011	-0.85	-0.17
B3-B1(250 y)	1000b Tg CH <sub>4</sub>	# 1 (108.4y)	+0.6 <sup>b</sup>	+0.0006 <sup>b</sup>	-0.05 <sup>b</sup>	-0.01 <sup>b</sup>
B3-B1(250 y)	10 Tg CH <sub>4</sub>	# 2 (10.1 y)	-0.007	-0.00005	+0.31	+10.4

<sup>a</sup>A<sup>#</sup>, integrated amplitudes; A, N<sub>2</sub>O-NO<sub>y</sub>-O<sub>3</sub>; B, N<sub>2</sub>O-NO<sub>y</sub>-O<sub>3</sub>-CH<sub>4</sub>. Numbers in parenthesis are model integration length in years in first column.

<sup>b</sup>The calculated perturbation B3 was computed with 10 Tg CH<sub>4</sub>, but here is scaled up to 1000 Tg-CH<sub>4</sub> to show the range of amplitudes in mode-1.



**Figure 2.** (top) Response to 10 Tg surface CH<sub>4</sub> emission perturbation (a) in globally-integrated total mass and (b) at equator at 31 km altitude in mole fraction. The straight dashed blue lines are the fitted mode-1 and mode-2 responses. Positive and negative amplitudes are plotted in solid and dashed lines respectively. (bottom) Mode amplitudes expressed in percentage relative to their steady-state control-run climatology. (c) Mode-1 is scaled arbitrarily to 10% perturbation to surface N<sub>2</sub>O (about 32 ppb). (d) Mode-2 is scaled arbitrarily to 10% perturbation to surface CH<sub>4</sub> (about 18 ppb).

so large that it takes over a hundred years to reverse sign and fall into the mode-1 pattern.

[14] The chemical eigenmodes are dimensionless multi-dimensional patterns of trace gas abundances, and perturbations to the different species in absolute abundance is determined by fixing one point. In Figures 2c and 2d we set the mean surface perturbations of N<sub>2</sub>O (mode-1) or CH<sub>4</sub> (mode-2) to +10% of the steady-state values and show the global, annual mean vertical profiles of the mode-1 abundances of N<sub>2</sub>O, NO<sub>y</sub>, O<sub>3</sub>, and CH<sub>4</sub> as % of their control-run profiles. With surface N<sub>2</sub>O at +10%, NO<sub>y</sub> is likewise about +10% throughout much of the stratosphere, the CH<sub>4</sub> perturbation increases from 0 in the lower stratosphere to -1% at the top. Ozone perturbations show a -2% peak near 35 km that is associated with ozone depletion from NO<sub>y</sub> catalytic cycles [Johnston, 1971] and a reversal to +1% around 20 km that combines NO<sub>y</sub>-mediated production of O<sub>3</sub> in the lower stratosphere along with radiative self-healing, i.e., the loss of O<sub>3</sub> above 25 km allows more photolysis of O<sub>2</sub> and hence production of O<sub>3</sub> below, as in the 1-D model [Prather, 1998]. For mode-2 (Figure 2d), a +10% surface CH<sub>4</sub> perturbation increases to +20% in the upper stratosphere and is associated with +1 to +2% increase in O<sub>3</sub> and N<sub>2</sub>O, especially in the upper stratosphere, but very small relative changes in NO<sub>y</sub>. Additional CH<sub>4</sub> slows down the

chlorine-catalyzed ozone loss above 35 km by reducing the ratio of ClO to HCl. The 2-D zonal mean spatial patterns of mode-1 and mode-2 for each species are shown in the Figure 1 of Text S1.

#### 4. Conclusion

[15] Using century-long simulations with a 3-D chemistry-transport model we have identified and separated the two longest-lived chemical modes associated with N<sub>2</sub>O and CH<sub>4</sub>. Mode-1 with an e-folding time of 108.4 y is a 3-D extension of the N<sub>2</sub>O-like mode previously found in a low-order system [Prather, 1998]. Like that study and the 2-D model studies of the decay of a N<sub>2</sub>O perturbation [Prather *et al.*, 2001, Table 4.5], we confirm that the mode-1 time scale is about 9% less than the atmospheric lifetime of N<sub>2</sub>O. The basic mode-1 time scale and spatial patterns of N<sub>2</sub>O, NO<sub>y</sub>, and O<sub>3</sub> abundances are similar in the chemical models with and without CH<sub>4</sub>, indicating that CH<sub>4</sub> chemical feedbacks are not crucial for the existence of the mode.

[16] The mode-2 time scale (10.1 y) is set by the parameterization of the tropospheric loss, and hence provides a simplistic form of the CH<sub>4</sub>-like mode found with realistic tropospheric chemistry [Wild and Prather, 2000]. Nevertheless, the coupled stratospheric chemistry of the (N<sub>2</sub>O-

$\text{NO}_y\text{-O}_3\text{-CH}_4\text{-H}_2\text{O}$ -system, as shown in the mode patterns, appears realistic in these calculations. Thus, the coupling of a  $\text{CH}_4$  perturbation to the 108.4-year mode-1 in these simulations should be representative of the atmosphere: a pulse of 100 Tg  $\text{CH}_4$  generates 0.1 Tg  $\text{N}_2\text{O}$  in mode-1.

[17] This study assesses how  $\text{CH}_4$  emissions, through stratospheric chemistry feedbacks, can change  $\text{N}_2\text{O}$ . From our results, we can calculate that the global warming of  $\text{CH}_4$  is effectively enhanced by the indirect effect of increasing  $\text{N}_2\text{O}$ , but this effect is small, increasing the GWP by about 1.2%. Another implication is for the observed, anthropogenic increases in both  $\text{CH}_4$  and  $\text{N}_2\text{O}$ . If one takes the anthropogenic flux of  $\text{CH}_4$  as 300 Tg/y, then about 4% of the anthropogenic flux of  $\text{N}_2\text{O}$  is due to this indirect chemistry. The reverse coupling, that of  $\text{N}_2\text{O}$  emissions to  $\text{CH}_4$ , requires full tropospheric chemistry that can respond to changes in overhead  $\text{O}_3$  column as well as the stratospheric influx of  $\text{O}_3$ . The simulations are much more computationally demanding and are now underway.

[18] Uncertainties should be assessed in CTM simulations such as these (e.g., resolution errors by Wild and Prather [2006]), but it remains a challenging task. However, the result that the mode-1 time relative to the  $\text{N}_2\text{O}$  lifetime is about 9% shorter appears to be robust across 1-, 2-, and 3-D models of varying chemical complexity. Uncertainty in the link between  $\text{CH}_4$  emissions and  $\text{N}_2\text{O}$ , i.e., a pulse of 100 Tg of  $\text{CH}_4$  generates 0.1 Tg of  $\text{N}_2\text{O}$ , calculated here for the first time, is even more difficult to assess: e.g., does it change with the mode-2 time? Does it depend on chlorine loading? In terms of importance for atmospheric composition and climate change, the largest uncertainties remain with the  $\text{CH}_4$  self-feedback (mode-2 time scale over  $\text{CH}_4$  lifetime) and the  $\text{N}_2\text{O}$  lifetime.

[19] **Acknowledgments.** We thank Geoffrey C. Toon at JPL NASA for pointing us to recent BOS-MkIV balloon measurement data set. The research is supported by NSF Atmospheric Chemistry (ATM-0550234) and the NASA MAP/GMI (NNG06GB84G).

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J. Hsu and M. J. Prather, Earth System Science, University of California, 3216 Croul Hall, Irvine, CA 92697, USA. (junoh@uci.edu)