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Lifetimes and eigenstates in atmospheric chemistry

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Abstract. The time scales and mode of the atmosphere's response to chemical perturbations are defined by the eigenvalues and eigenvectors of the system. The eigenstates of a simplified one-box CH_4-CO-OH system are analyzed. The longest time constant (smallest eigenvalue) always exceeds the lifetime defined by the steady-state loss frequency for CH_4, the longest lived gas. Thus, the extent of a CH_4 perturbation—the methane response time—is always longer than predicted by the steady-state lifetime and is independent of size of the perturbation in the linear limit. This lengthening of the atmospheric recovery time can be diagnosed by how close we are to a chemically unstable troposphere, i.e., how much OH production exceeds that minimum needed to oxidize just the global emissions of CH_4, CO, and other hydrocarbons and species.

Introduction

The definition of a lifetime in atmospheric chemistry carries meaning insofar as it represents a fundamental time constant of the chemical system. The inverse of the atmospheric "lifetime", a loss frequency, is usually defined as the globally, annually integrated loss rate of a compound divided by its total burden. In steady state this burden divided by the "lifetime" is equal to the sources needed to maintain current abundances. Policy makers considering the potential environmental damage of a compound must know how long a perturbation will last. Recently, Don Fisher (AFEAS/NASA/NOAA Workshop, Boulder, CO, 17-19 Nov 1993) questioned the application of the traditionally defined lifetimes for CH_4 in climate assessments [e.g., *Houghton et al.*, 1992] because he found that CH_4 perturbations in his global model decayed more slowly than implied by the "lifetime" and that this response time was similar for infinitesimal and for small amplitude (<20%) perturbations.

It has been long noted that the tropospheric CH_4-CO-OH system is highly coupled [*Chameides et al.*, 1976; *Sze*, 1977] and that the apparent time scale for a perturbation to decay is longer that any of the lifetimes of the three components as defined above. Here I show that the decomposition of a simplified, one-box CH_4-CO-OH system into eigenvalues and eigenvectors yields eigenvalues (i.e., inverse times) that differ from the more obviously defined lifetimes derived from the instantaneous loss frequencies. This new approach is consistent with other studies of simplified CH_4-OH systems [*Guthrie*, 1989; *Prather*, 1989; *Wigley and Osborn*, 1994] and with more detailed global modeling studies [*Isaksen and Hov*, 1987] in which OH feedback affects the lifetime of CH_4. Sensitivity analysis here shows that one key factor explains the extended "lifetime" for CH_4 perturbations: the excess source of tropospheric OH relative to the source of CH_4 and CO that must be oxidized by OH. This factor provides a simple diagnostic that may be used to understand the more complex 3-D tropospheric chemical models for which the calculation of such eigenstates would be exceedingly difficult.

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Chemical System

Atmospheric chemistry is complex and four dimensional, varying with time over latitude, longitude, and altitude. The true chemical eigenstates of the atmosphere depend not only on local chemical rates but also on the rates of transport that redistribute chemicals throughout the troposphere and stratosphere. For example, a typical methane (CH_4) molecule will travel through much of the atmosphere during its 10-year lifetime, including the stratosphere, before it is destroyed by reaction with hydroxyl (OH) radicals. The calculation of eigenstates requires knowledge of the transport "coefficients" as well as the chemical rate coefficients. For this analysis we collapse the atmosphere into a single box and average transport terms and missing chemistry into fixed source terms. The purpose here is to identify the key component that controls the eigenstate time scales.

The chemical reactions of the CH_4-CO-OH system considered here are

$$\mathrm{OH} + \mathrm{CH_4} \Rightarrow \text{(multiple steps)} \Rightarrow \mathrm{CO} + \text{products} \quad (1)$$

$$\mathrm{OH} + \mathrm{CO} \Rightarrow \mathrm{CO_2} + \mathrm{H} \quad (2)$$

$$\mathrm{OH} + \mathrm{X} \Rightarrow \text{products} \quad (3)$$

with rates

$$R_1 = k_1\,[\mathrm{OH}]\,[\mathrm{CH_4}] \quad (4)$$

$$R_2 = k_2\,[\mathrm{OH}]\,[\mathrm{CO}] \quad (5)$$

$$R_3 = k_3\,[\mathrm{OH}]\,[\mathrm{X}]. \quad (6)$$

The only product we are concerned with is the production of CO in R_1. The inclusion of surrogate X allows for OH sinks that are independent of the CH_4-CO system. The time-dependent equations describing the concentrations $[CH_4]$, [CO], and [OH] are then,

$$d[\mathrm{CH_4}]/dt = S_{CH4} - R_1 \quad (7)$$

$$d[\mathrm{CO}]/dt = S_{CO} + R_1 - R_2 \quad (8)$$

$$d[\mathrm{OH}]/dt = S_{OH} - R_1 - R_2 - R_3 \quad (9)$$

where constant source terms (S) for each species are included. At steady state (i.e., d[ ]/dt = 0), $R_1 = S_{CH4}$ and then $R_2 = S_{CO} + S_{CH4}$. Thus positive solutions for [OH] occur only if $S_{OH} > 2\times S_{CH4} + S_{CO}$, i.e., the source of OH must be large enough to oxidize combined sources of CH_4 and CO.

The solution of this system at steady-state is trivial, and an example is given in the Table. In this example, the rate coefficients and sources were chosen to be typical of values in the lower troposphere, and the resulting $[CH_4]$ and [CO] are slightly, about 25%, higher than currently observed in the northern hemisphere.

Eigenstates

Let V be a solution vector $\{CH_4, CO, OH\}$ to $dV/dt = A(V)$ where the matrix operator A(V) represents equations (7-9) evaluated at V. Then a perturbed state $V+\delta V$ can be solved as a linear expansion,

$$\begin{aligned} d(V+\delta V)/dt &= dV/dt + d\delta V/dt \\ &= A(V+\delta V) \approx A(V) + \mathbf{J}\,\delta V, \end{aligned} \qquad (10)$$

where the Jacobian (**J**) of the 3×3 system **A** is defined as the partial derivatives of the rate-of-change equations(7-9):

$$\begin{matrix} \frac{\partial(d[CH_4]/dt)}{\partial[CH_4]} & \frac{\partial(d[CH_4]/dt)}{\partial[CO]} & \frac{\partial(d[CH_4]/dt)}{\partial[OH]} \\ \frac{\partial(d[CO]/dt)}{\partial[CH_4]} & \frac{\partial(d[CO]/dt)}{\partial[CO]} & \frac{\partial(d[CO]/dt)}{\partial[OH]} \\ \frac{\partial(d[OH]/dt)}{\partial[CH_4]} & \frac{\partial(d[OH]/dt)}{\partial[CO]} & \frac{\partial(d[OH]/dt)}{\partial[OH]} \end{matrix} \qquad (11)$$

The eigenstates of **J** describe the behavior of the system for infinitesimal perturbations about this state. If δV is an eigenvector of **J** with eigenvalue e (<0), then from equation (10), $d(\delta V)/dt = \mathbf{J}\,\delta V = e\,\delta V$, and the perturbation decays, $\delta V(t) = \delta V(t=0)\,e^{et}$, with time scale of 1/e. An example is given in the Table. If the chemistry were nearly linear, then the Jacobian would be diagonally dominant and the eigenvalues would be equal to the diagonal elements, i.e., the instantaneous loss frequencies. Because the CH_4-CO-OH system is highly coupled, the Jacobian is not diagonally dominant.

Table 1. Solution and Eigenstates

$k1 = 5.0\times10^{-15}\ cm^3s^{-1}$ * $S_{CH4} = 1.6\times10^5\ cm^{-3}s^{-1}$
$k_2 = 2.0\times10^{-13}\ cm^3s^{-1}$ * $S_{CO} = 2.4\times10^5\ cm^{-3}s^{-1}$
$k_3[X] = 1\ s^{-1}$ $S_{OH} = 11.2\times10^5\ cm^{-3}s^{-1}$
* typical tropospheric values (**E** = 1)

Solution at steady-state (cm^{-3}):
$[CH_4] = 5.714\times10^{13}$ $[CO] = 3.571\times10^{12}$ $[OH] = 5.60\times10^5$

Jacobian matrix ($\mathbf{J}_{ij}$) for steady-state solution (s^{-1}):

-2.80×10^{-9}	0.0	-0.285714
$+2.80\times10^{-9}$	-1.12×10^{-7}	-0.428571
-2.80×10^{-9}	-1.12×10^{-7}	-2.000000

Eigenvalues (s^{-1}):	e_1	e_2	e_3
	-1.769135×10^{-9}	-8.863086×10^{-8}	-2.000000
	(1 / 18 y)	(1 / 131 d)	(1 / 0.5 s)

Eigenvectors (cm^{-3}):	$\mathbf{v}_1$	$\mathbf{v}_2$	$\mathbf{v}_3$
$\Delta[CH_4]$	+0.999	-0.182	-0.138
$\Delta[CO]$	+0.039	+0.983	-0.208
$\Delta[OH]$	-3.6×10^{-9}	-5.5×10^{-8}	-0.968

Eigenvectors (% of steady-state solution):

$\mathbf{v}_1$	$\mathbf{v}_2$	$\mathbf{v}_3$	
100.0	-1.2	0.000000	$\Delta[CH_4]/[CH_4]_{s-s}$
+63.1	100.0	0.000003	$\Delta[CO]/[CO]_{s-s}$
-36.8	-35.6	100.0	$\Delta[OH]/[OH]_{s-s}$

Coefficients of eigenvectors for single perturbation to:

	$\times\mathbf{v}_1$	$\times\mathbf{v}_2$	$\times\mathbf{v}_3$
$\Delta[CH_4]=1$:	+0.994	-0.040	-1.4×10^{-9}
$\Delta[CO]=1$:	+0.184	+1.010	-5.8×10^{-8}
$\Delta[OH]=1$:	-0.181	-0.211	-1.033

The CH_4 instantaneous loss frequency, $-2.80\times10^{-9}\ s^{-1}$, is given by the diagonal element corresponding to $\partial(d[CH_4]/dt)/\partial[CH_4]$. This apparent atmospheric "lifetime" of 11.3 y is much shorter than the time constant defined by the inverse of eigenvalue e_1, 17.9 y. Because **J** is asymmetric, the eigenvectors are not orthogonal, but they do form a linearly independent basis set. Thus, any perturbation to the system can be uniquely decomposed into a combination of these three eigenvectors, each of which decays with its own time constant. Eigenvectors may be normalized arbitrarily, and a unit-length (defined by the 2-norm) with physical units of cm^{-3} is chosen here.

As shown in the Table, the first eigenvector $\mathbf{v}_1$ corresponds to perturbations that decay with this 17.9-year time scale and is expressed primarily as a CH_4 perturbation, but with comparable (%) changes in CO and OH. The second eigenvector $\mathbf{v}_2$ corresponds mostly to a coupled CO-OH state. The third eigenvector $\mathbf{v}_3$ is solely an OH perturbation. Also shown in the Table, a perturbation to $[CH_4]$ alone is decomposed primarily into the first eigenvector, $\mathbf{v}_1$, ($1/e_1$ = 17.9 y) and secondarily into $\mathbf{v}_2$ ($1/e_2$ = 0.36 y). Note, however, that the primary eigenvector includes a +63% perturbation to [CO] and a -37% change in [OH] for a $[CH_4]$-perturbation of +100%. Perturbations to [CO] and [OH] are primarily represented by their principle eigenvectors $\mathbf{v}_2$ and $\mathbf{v}_3$, respectively. In addition, both also excite $\mathbf{v}_1$, an atmospheric perturbation with a 17.9-year time constant, a consequence noted by Sze [1977].

Sensitivity Analysis

Let us consider the two obvious independent variables: the third-party OH loss, $k_3[X]$; and the excess source of OH,

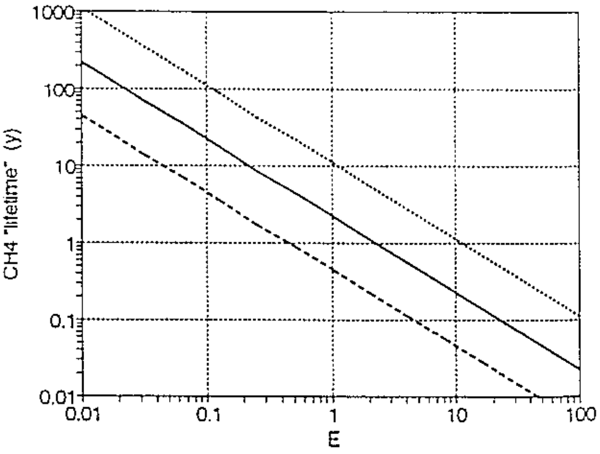

Figure 1. Steady-state "lifetime" for CH_4 ($-1/J_{11}$) as a function of E, the excess source of OH (see text). The "lifetime" is defined from the loss frequency for CH_4 and is computed for the CH_4 and CO source values of Table 1. Shown are three curves for values of $k_3[X]$ = 0.04 (dashed), 0.20 (solid), and 1.00 (dotted).

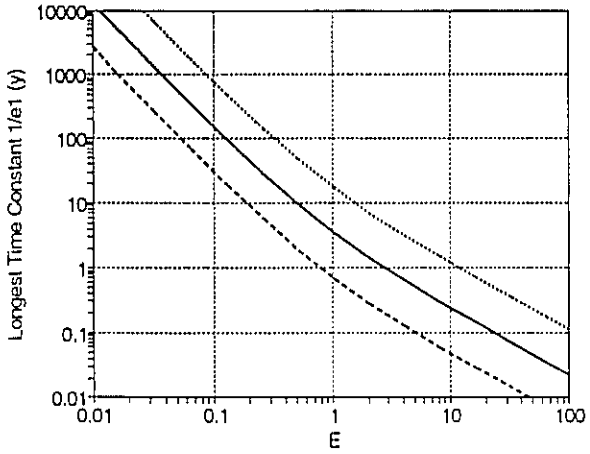

Figure 2. Eigenvalue time constant ($-1/e_1$) as a function of E. e_1 is the longest time constant of the system. See Fig. 1.

$E = S_{OH}/(2 \times S_{CH4}+S_{CO}) - 1$. The apparent "lifetime" for CH_4, $-1/J_{11}$, and the longest time constant of the coupled system, $-1/e_1$, are shown as functions of E in Figures 1 & 2, respectively. The "lifetime" varies linearly with E on a log-log plot as expected, and the change for different values of $k_3[X]$ is shown to be similarly linear. The logarithm of $-1/e_1$ does not behave similarly; indeed, it becomes singular as $E \rightarrow 0$. Figure 3 shows the ratio of time constants, J_{11}/e_1; for $E > 10$ the two values are almost identical; for $E < 0.1$ the ratio is greater than 7. Note that the dependence on $k_3[X]$ has vanished and that the lengthening of the CH_4 time constant, the ratio J_{11}/e_1, depends solely on E. This ratio of response time to "lifetime" for these equations is equal to the sensitivity of OH decrease with respect to CH_4 increase, $1/(1+\partial \ln[OH]/\partial \ln[CH_4])$, as defined in global models [e.g., *Isaksen and Hov*, 1987].

Another independent variable must be recognized: $S_{CH4}/(2 \times S_{CH4}+S_{CO})$, the fraction of total CH_4-CO source that begins as CH_4. This variable affects only the partitioning of CH_4 and CO abundances and not the value of OH or the chemical "lifetimes". It does affect the ratio J_{11}/e_1 as shown in Figure 3; however, the choice among curves in Figure 3 can be made easily from the observed relative abundances of CH_4 and CO, assuming we know there relative rate coefficients, k_1/k_2. For example, CH_4 concentrations of 1700 ppb and CO concentrations ranging from 50 to 100 ppb would restrict us to the top two curves.

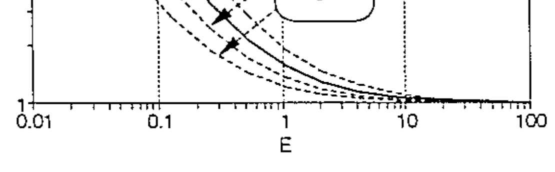

Figure 3. Ratio of time constants for CH_4 (J_{11}/e_1) as a function E. The curves for different $k_3[X]$ collapse onto the solid line (See Figure 1). A new family of curves shows the dependence on relative sources of CH_4 and CO: $S_{CH4}/(S_{CO}+2 \times S_{CH4})$ values from 0.46, 0.29, 0.18, 0.11 result in the labeled $[CH_4]/[CO]$ ratios of 35, 16, 9, and 5, respectively.

The largest eigenvalue e_3 corresponds to the OH time constant. Figure 4 shows $-1/e_3$ as functions of $k_3[X]$ and E. In this figure the OH lifetime, $-1/J_{33}$, is indistinguishable from $-1/e_3$. When $E > 10$ the system is not highly coupled and the OH lifetime asymptotes to the third-party loss frequency, $1/k_3[X]$.

Figure 5 shows the components of the eigenvector v_1 as a function of E, for $k_3[X] = 1.00$. In these cases, the absolute eigenvectors (cm^{-3}) have been scaled to relative perturbations with respect to the steady-state solution. In the highly non-linear regime ($E < 0.1$) a perturbation to CH_4 is matched by a comparable (in %) perturbation to CO and an equally large but opposite perturbation to OH. As the system becomes linear ($E > 10$), the OH-component disappears from v_1 and the CO-component reduces to that fraction of CO source derived from oxidation of CH_4, i.e., 40% in this case.

Conclusion

In today's atmosphere the CH_4-CO-OH system has time constants that differ from the "lifetimes", and hence infinitesimal perturbations will respond with the eigenvalue frequencies. Even if the system is not in steady state, small amplitude perturbations to long-term trends will decay with the eigenvalue time constants (see equation 10). Large-amplitude perturbations, however, will decay on a time scale differing from both the chemically defined "lifetime" and the inverse of the eigenvalue frequencies. Such time scales are most easily estimated by numerical simulation of the non-linear equations (because the Jacobian is not a constant). The critical factor causing a difference between the "lifetime" and the eigenstate time constants (i.e., the response times) is the amount of non-linearity in the chemistry. For a compound such as CH_3CCl_3 with small absolute impact on the CO-OH system, its associated eigenvalue is well approximated by the "lifetime" calculated from the average loss frequency.

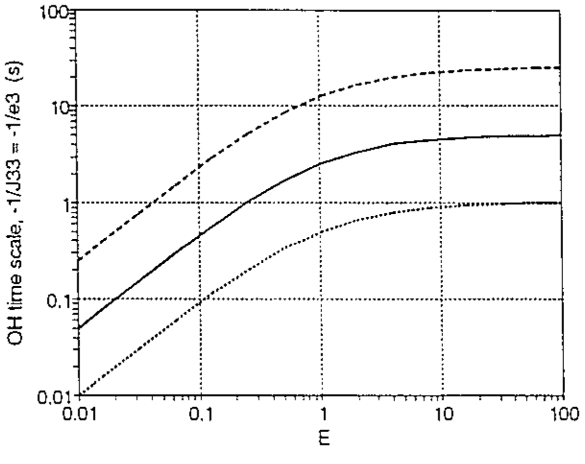

Figure 4. Steady-state "lifetime" for OH ($-1/J_{33}$) as a function E. The values of $-1/e_3$, the largest eigenvalue, are indistinguishable. See Figure 1.

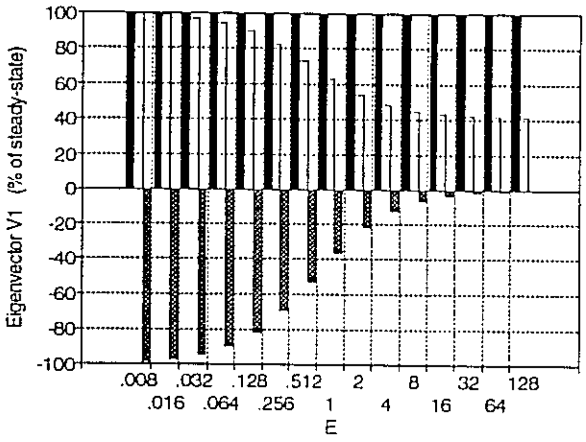

Figure 5. Eigenvectors v_1 associated with eigenvalue e_1 as a function of E. The eigenvectors are scaled to the percent of the steady-state values for CH_4 (dark bars), CO (white) and OH (gray), see Table.

In the example here the key factor controlling the ratio of the CH_4 eigenvalue time constant to the lifetime, J_{11}/e_1, is the excess source of OH relative to that of CH_4 and CO. The source term S_{OH} integrates not only the primary production of OH

$$O_3 + \text{photon} \Rightarrow O(^1D) + O_2 \qquad (12)$$

$$O(^1D) + H_2O \Rightarrow OH + OH \qquad (13)$$

but also reactions which recycle HO_2 radicals and H_2O_2 back to OH, particularly

$$HO_2 + NO \Rightarrow OH + NO_2 \qquad (14)$$

$$H_2O_2 + \text{photon} \Rightarrow OH + OH. \qquad (15)$$

In the upper troposphere with sufficient NO concentrations, addition of CH_4 can enhance OH (a feedback not included here) because more than one HO_2 radical is produced during the oxidation of the CH_3 radical. One expects that global tropospheric chemistry models may differ substantially in the CH_4-CO-OH coupling because of the differing NO_x fields.

Individual 3-D chemical models may be able to diagnose the longest eigenvalue in the system by perturbing CH_4 and then watching the decay of all the excited eigenstates. However, the ability to disentangle different eigenstates, or to understand why models differ, or to evaluate uncertainties will not be easy. Thus a simple diagnostic of the nonlinearity in tropospheric chemistry would be the E factor defined here, extended to include the oxidation of other hydrocarbons. Since we are looking for time constants longer than one year, the S_{OH} term must be integrated annually over the global 3-D chemical fields and compared with the source of CH_4, CO, and other hydrocarbons.

The factor E is a measure of how close the troposphere is to chemical instability: when E is less than zero, there is not enough oxidizing power to remove the emissions of CH_4, CO, other species. However, the source of OH is not fixed and can respond to enhanced CH_4 and CO levels through reactions (14-15); and in regions where $E < 0$, such as high latitude winter, the emissions will be balanced by seasonal transport to lower latitudes where more OH is produced. Also, stratospheric loss, with an effective lifetime of about 120 yr, provides a sink for atmospheric CH_4 that does not feed back as does tropospheric OH. A more accurate evaluation, integrating over all these conditions and local variations in E, must be made with global chemical transport models.

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References

Chameides, W. L., S. C. Liu, and R. J. Cicerone, Possible variations in atmospheric methane, *J. Geophys. Res., 81*, 4997-5001, 1976.

Guthrie, P. D., The CH_4-CO-OH conundrum: a simple analytic approach, *Global Biogeochemical Cycles, 3*, 287-298, 1989.

Houghton, J. T., B. A. Callander, and S. K. Varney, eds., *Climate Change 1992: The Supplementary Report to the IPCC Scientific Assessment*, 200 pp., Cambridge U. Press, Cambridge, UK, 1992.

Isaksen, I. S. A., and Ø. Hov, Calculation of trends in the tropospheric concentration of O_3, OH, CH_4, and NO_x, *Tellus, 39B*, 271-285, 1987.

Prather, M. J., ed., An Assessment Model for Atmospheric Composition, *NASA Conference Publication, CP-3203*, 64 pp, Washington, DC, 1989.

Sze, N. D., Anthropogenic CO emissions: implications for the atmospheric CO-OH-CH4 cycle, *Science, 195*, 673-675, 1977.

Wigley, T. M. L. and T. J. Osborn, Indirect global warming potentials for CH_4 due to OH feedback, *Geophys. Res. Lett.*, in press, 1994.

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