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 CH₄-CO-OH system are analyzed. The longest time constant (smallest eigenvalue) always exceeds the lifetime defined by the steady-state loss frequency for CH₄, the longest lived gas. Thus, the extent of a CH₄ 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 CH₄, 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 (AFEFAS/ NASA/NOAA Workshop, Boulder, CO, 17-19 Nov 1993) questioned the application of the traditionally defined lifetimes for CH₄ in climate assessments [e.g., Houghton et al., 1997] because he found that CH₄ 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 CH₄ 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 than any of the lifetimes of the three components as defined above. Here I show that the decomposition of a simplified, one-box CH₄-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 CH₄-OH systems [Guthrie, 1989; Prather, 1989; Wigley and Osborn, 1994] and with more detailed global modeling studies [Isaksen and Ilov, 1987] in which OH feedback affects the lifetime of CH₄. Sensitivity analysis here shows that one key factor explains the extended "lifetime" for CH₄ perturbations: the excess source of tropospheric OH relative to the source of CH₄ 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.

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 (CH₄) 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 CH₄-CO-OH system considered here are

\[ \text{OH} + \text{CH}_4 \rightarrow \text{(multiple steps) } \rightarrow \text{CO} + \text{products} \]

\[ \text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H} \]

\[ \text{OH} + \text{X} \rightarrow \text{products} \]

with rates

\[ R_1 = k_1 [\text{OH}] [\text{CH}_4] \]

\[ R_2 = k_2 [\text{OH}] [\text{CO}] \]

\[ R_3 = k_3 [\text{OH}] [\text{X}] \]

The only product we are concerned with is the production of CO in R₁. The inclusion of surrogate X allows for OH sinks that are independent of the CH₄ CO system. The time-dependent equations describing the concentrations \([\text{CH}_4], [\text{CO}], \text{and [OH]}\) are then,

\[ \frac{d[\text{CH}_4]}{dt} = S_{\text{CH}_4} - R_1 \]

\[ \frac{d[\text{CO}]}{dt} = S_{\text{CO}} + R_1 - R_2 \]

\[ \frac{d[\text{OH}]}{dt} = S_{\text{OH}} - R_1 - R_2 - R_3 \]

where constant source terms \((S)\) for each species are included. At steady state (i.e., \(d[\text{X}] / dt = 0\), \(R_1 = S_{\text{CH}_4}\) and then \(R_2 = S_{\text{CO}} + S_{\text{CH}_4}\). Thus positive solutions for [OH] occur only if \(S_{\text{OH}} > 2 \times S_{\text{CH}_4} + S_{\text{CO}}\), i.e., the source of OH must be large enough to oxidize combined sources of CH₄ 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 [CH₄] and [CO] are slightly, about 25%, higher than currently observed in the northern hemisphere.

**Eigenstates**

Let V be a solution vector \{CH₄,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 + δV can be solved as a linear expansion,

\[
d(V + δV)/dt = dV/dt + δdV/dt = A(V + δV) = A(V) + J δV,
\]

where the Jacobian (J) of the 3x3 system A is defined as the partial derivatives of the rate-of-change equations (7-9):

\[
\begin{align*}
\frac{d}{d[M]} & = \frac{d[CH_4]}{d[CH_4]} \frac{d[CH_4]}{d[CO]} \frac{d[CH_4]}{d[OH]} \\
\frac{d[CO]}{d[CH_4]} & = \frac{d[CO]}{d[CO]} \frac{d[CO]}{d[CO]} \frac{d[CO]}{d[CO]} \\
\frac{d[OH]}{d[CH_4]} & = \frac{d[OH]}{d[CO]} \frac{d[OH]}{d[CO]} \frac{d[OH]}{d[CO]}
\end{align*}
\]

(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 ε (<0), then from equation (10), d(δV)/dt = J δV = ε δV, and the perturbation decays, δV(t) = δV(t=0) e^(-t/ε), with time scale of 1/ε. 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 CH₄-CO-OH system is highly coupled, the Jacobian is not diagonally dominant.

The CH₄ instantaneous loss frequency, -2.80×10⁻⁹ s⁻¹, is given by the diagonal element corresponding to d[CH₄]/dt)/d[CH₄]. This apparent atmospheric "lifetime" of 11.3 y is much shorter than the time constant defined by the inverse of eigenvalue ε₁, 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 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 v₁ corresponds to perturbations that decay with this 17.9-year time scale and is expressed primarily as a CH₄ perturbation, but with comparable (%) changes in CO and OH. The second eigenvector v₂ corresponds mostly to a coupled CO-OH state. The third eigenvector v₃ is solely an OH perturbation. Also shown in the Table, a perturbation to [CH₄] alone is decomposed primarily into the first eigenvector, v₁ (1/ε₁ = 17.9 y) and secondarily into v₂ (1/ε₂ = 0.36 y). Note, however, that the primary eigenvalue includes a +63% perturbation to [CO] and a -37% change in [OH] for a CH₄-perturbation of +100%. Perturbations to [CO] and [OH] are primarily represented by their principle eigenvectors v₂ and v₃, respectively. In addition, both also excite v₁, an atmospheric perturbation with a 17.9-year time constant, a consequence noted by Sze [1977].

### Table 1. Solution and Eigenstates

<table>
<thead>
<tr>
<th>k₁</th>
<th>k₂</th>
<th>k₃[X]</th>
<th>k₄[CH₄]</th>
<th>k₅[CO]</th>
<th>k₆[OH]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0×10⁻¹⁵ cm³ s⁻¹</td>
<td>2.0×10⁻¹⁵ cm³ s⁻¹</td>
<td>1 s⁻¹</td>
<td>SCH₄ = 1.6×10⁻⁵ cm⁻³ s⁻¹</td>
<td>SCO = 2.4×10⁻⁵ cm⁻³ s⁻¹</td>
<td>SOH = 11.2×10⁻⁵ cm⁻³ s⁻¹</td>
</tr>
</tbody>
</table>

*Typical tropospheric values (K = 1)*

### Solution at steady-state (cm⁻³):

[CH₄] = 5.714×10¹³ [CO] = 3.571×10¹² [OH] = 5.60×10⁵

### Jacobian matrix (J)| for steady-state solution (s⁻¹):

<table>
<thead>
<tr>
<th>v₁</th>
<th>v₂</th>
<th>v₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2.80×10⁻⁹</td>
<td>+1.12×10⁻⁷</td>
<td>-1.12×10⁻⁷</td>
</tr>
<tr>
<td>+2.80×10⁻⁹</td>
<td>-1.12×10⁻⁷</td>
<td>-1.12×10⁻⁷</td>
</tr>
<tr>
<td>-2.80×10⁻⁹</td>
<td>-1.12×10⁻⁷</td>
<td>-2.00000</td>
</tr>
</tbody>
</table>

### Eigenvalues (s⁻¹): ε₁ | ε₂ | ε₃

-1.769135×10⁻⁹ | -8.863086×10⁻⁸ | -2.00000

(1 / 18 y) | (1 / 131 d) | (1 / 0.5 s)

### Eigenvalues (cm⁻³): ΔCH₄ | ΔCO | ΔOH

v₁ | v₂ | v₃

+0.999 | -0.182 | -0.138

ΔCH₄ | ΔCO | ΔOH

+0.039 | +0.983 | -0.208

-3.6×10⁻⁹ | -5.5×10⁻⁸ | -0.968

### Eigenvectors (% of steady-state solution):

<table>
<thead>
<tr>
<th>v₁</th>
<th>v₂</th>
<th>v₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>100.0</td>
<td>1.2</td>
<td>0.000000</td>
</tr>
<tr>
<td>+63.1</td>
<td>100.0</td>
<td>0.000000</td>
</tr>
<tr>
<td>-36.8</td>
<td>-35.6</td>
<td>100.0</td>
</tr>
</tbody>
</table>

### Coefficients of eigenvectors for single perturbation to:

<table>
<thead>
<tr>
<th>ΔCH₄</th>
<th>ΔCO</th>
<th>ΔOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.994</td>
<td>0.40</td>
<td>1.4×10⁻⁹</td>
</tr>
<tr>
<td>0.184</td>
<td>+1.010</td>
<td>-5.8×10⁻⁸</td>
</tr>
<tr>
<td>-0.181</td>
<td>-0.211</td>
<td>-1.033</td>
</tr>
</tbody>
</table>

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**Sensitivity Analysis**

Let us consider the two obvious independent variables: the third-party OH loss, k₃[X]; and the excess source of OH.

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**Figure 1.** Steady-state "lifetime" for CH₄ (1/t₁₁₁) as a function of E, the excess source of OH (see text). The "lifetime" is defined from the loss frequency for CH₄ and is computed for the CH₄ and CO source values of Table 1. Shown are three curves for values of k₃[X] = 0.04 (dashed), 0.20 (solid), and 1.00 (dotted).
E = \frac{S_{\text{OH}}/(2xS_{\text{CH}_4}+S_{\text{CO}})}{1}. The apparent "lifetime" for \text{CH}_4, -1/s_{\text{CH}_4}, 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_2[X] is shown to be similarly linear. The logarithm of -1/e_1 does not behave similarly, indeed, it becomes singular as E \to 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_2[X] has vanished and that the lengthening of the \text{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 \text{CH}_4 increase, 1/((1+2\ln(\text{OH})/2\ln(\text{CH}_4))), as defined in global models [e.g., Isaksen and Hov, 1987].

Another independent variable must be recognized: \frac{S_{\text{CH}_4}}{S_{\text{CO}}+2xS_{\text{CH}_4}}, the fraction of total \text{CH}_4–\text{CO} source that begins as \text{CH}_4. This variable affects only the partitioning of \text{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 \text{CH}_4 and CO, assuming we know there relative rate coefficients, k_2/k_1. For example, \text{CH}_4 concentrations of 1700 ppb and CO concentrations ranging from 50 to 100 ppb would restrict us to the top two curves.

The largest eigenvalue e_1 corresponds to the OH time constant. Figure 4 shows -1/e_2 as functions of k_2[X] and E. In this figure the OH lifetime, -1/J_{33}, is indistinguishable from -1/e_2. When E > 10 the system is not highly coupled and the OH lifetime asymptotizes 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_2[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 \text{CH}_4 is matched by a comparable (in %) perturbation to CO and an equally large but opposite perturbation to OII. 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 \text{CH}_4, i.e., 40% in this case.

**Conclusion**

In today's atmosphere the \text{CH}_4-CO-OII 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 nonlinear 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 \text{CH}_3\text{CCl}_3 with small absolute impact on the CO-OII system, its associated eigenvalue is well approximated by the "lifetime" calculated from the average loss frequency.
Figure 5. Eigenvectors \( \mathbf{v}_1 \) associated with eigenvalue \( \epsilon_1 \) as a function of \( E \). The eigenvectors are scaled to the percent of the steady-state values for \( \text{CH}_4 \) (dark bars), \( \text{CO} \) (white) and \( \text{OH} \) (gray), see Table.

In the example here the key factor controlling the ratio of the \( \text{CH}_4 \) eigenvalue time constant to the lifetime, \( J_1/\epsilon_1 \), is the excess source of \( \text{OH} \) relative to that of \( \text{CH}_4 \) and \( \text{CO} \). The source term \( S_{\text{OH}} \) integrates not only the primary production of \( \text{OH} \)

\[
O_3 + \text{photon} \Rightarrow O(^1D) + O_2 \quad (12)
\]

\[
O(^1D) + H_2O \Rightarrow OH + OH \quad (13)
\]

but also reactions which recycle \( \text{HO}_2 \) radicals and \( H_2O_2 \) back to \( \text{OH} \), particularly

\[
\text{HO}_2 + \text{NO} \Rightarrow \text{OH} + \text{NO}_2 \quad (14)
\]

\[
H_2O_2 + \text{photon} \Rightarrow \text{OH} + \text{OH}. \quad (15)
\]

In the upper troposphere with sufficient \( \text{NO} \) concentrations, addition of \( \text{CH}_4 \) can enhance \( \text{OH} \) (a feedback not included here) because more than one \( \text{HO}_2 \) radical is produced during the oxidation of the \( \text{CH}_4 \) radical. One expects that global tropospheric chemistry models may differ substantially in the \( \text{CH}_4-\text{CO}-\text{OH} \) coupling because of the differing \( \text{NO}_X \) fields.

Individual 3-D chemical models may be able to diagnose the longest eigenvalue in the system by perturbing \( \text{CH}_4 \) 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 non-linearity 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 \( S_{\text{OH}} \) term must be integrated annually over the global 3-D chemical fields and compared with the source of \( \text{CH}_4 \), \( \text{CO} \), 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 \( \text{CH}_4 \), \( \text{CO} \), other species. However, the source of \( \text{OH} \) is not fixed and can respond to enhanced \( \text{CH}_4 \) and \( \text{CO} \) 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 \( \text{OH} \) is produced. Also, stratospheric loss, with an effective lifetime of about 120 yr, provides a sink for atmospheric \( \text{CH}_4 \) that does not feed back as does tropospheric \( \text{OH} \). A more accurate evaluation, integrating over all these conditions and local variations in \( E \), must be made with global chemical transport models.

Acknowledgements. I would like to thank Don Fisher for raising this important issue regarding climate assessments of methane, and for reminding me of discussions long ago with Nlen Dak Sze and others at Harvard University regarding the \( \text{CH}_4-\text{CO}-\text{OH} \) instability. The work of two anonymous reviewers is also appreciated. This work was supported by the Atmospheric Chemistry Programs of NSF and NASA.

References


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