ラジカル素反応過程と大気と燃焼の科学

東京大学 大学院工学系研究科 化学システム工学専攻

三好 明

「プラズマ科学における分光計測の高度化と原子分子過程研究の新展開」
「原子分子データ応用フォーラムセミナー」合同研究会 (2016年12月21日 核融合研究所/土岐)

はじめに

私 (三好 明)

専門：化学反応論・燃焼化学・大気化学

1990　工学博士 (東京大学・反応化学専攻)
1990– 環境庁 国立環境研究所 大気圏環境部 研究員
1992– 東京大学 工学部 反応化学科 助手
2000– 東京大学 大学院工学系研究科 化学システム工学専攻
准教授

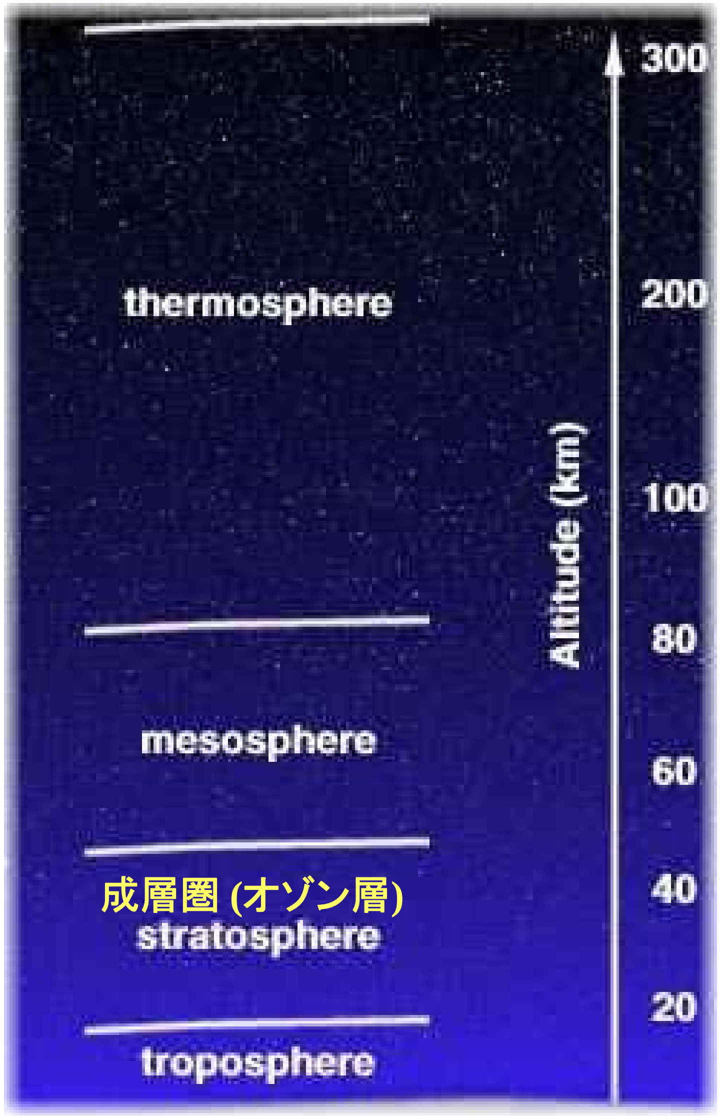
詳細：*http://www.frad.t.u-tokyo.ac.jp/*

オゾン層破壊

Ozone Depletion

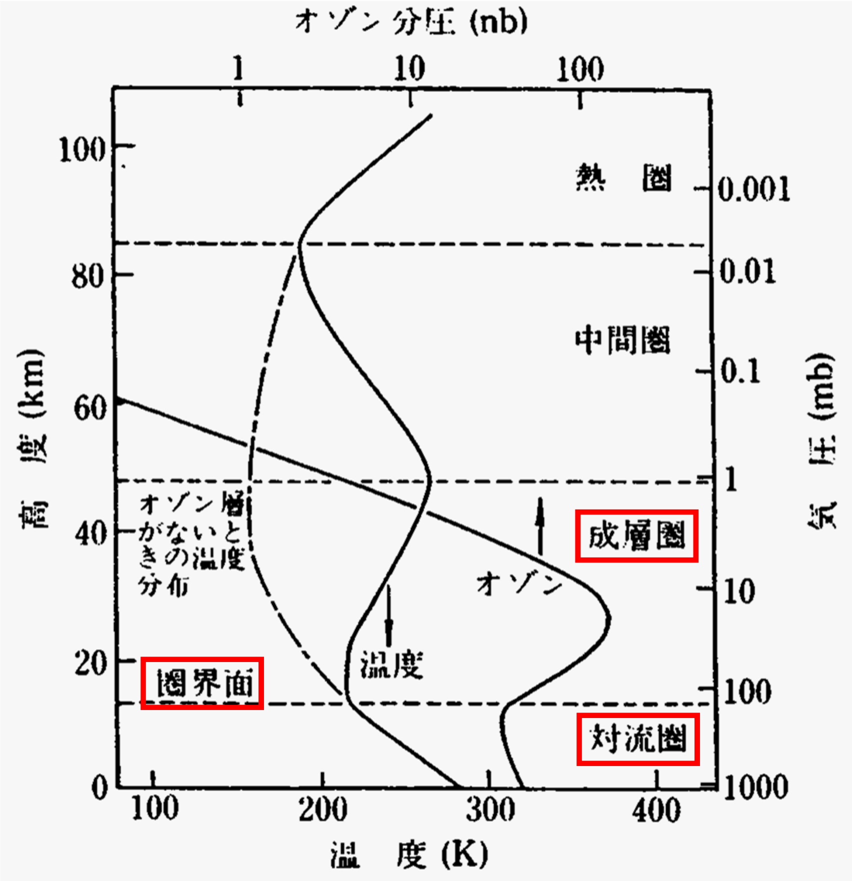
— 地球規模環境問題への
対策の優等生

地球大気の構造



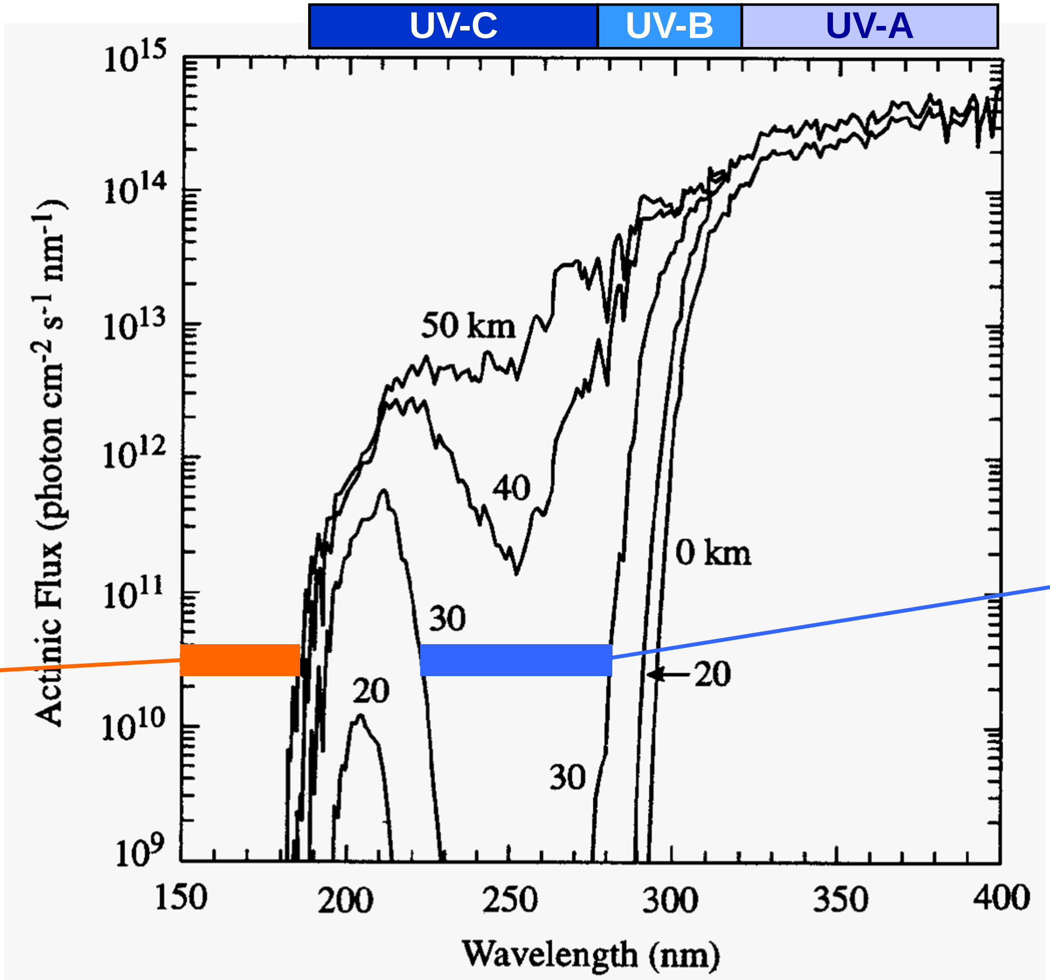
https://science.nasa.gov/ (2000)

大気の >99% は成層圏・
対流圏に存在



"フロン 地球を蝕む物質," 富永 健, 巻出 義紘,
F. S. Rowland, 東大出版会, 東京 (1990).

太陽光の波長分布



酸素 (O_2)
による吸収

オゾン (O_3)
による吸収

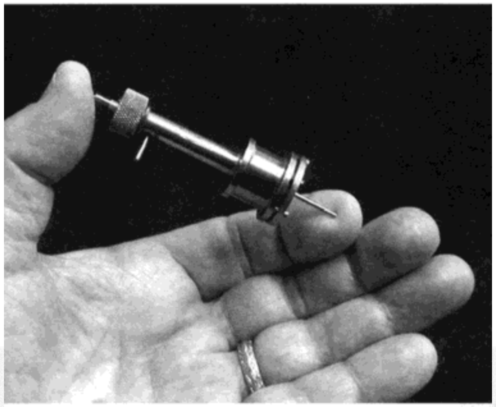
Fig. 10-2 Solar actinic flux at different altitudes, for typical atmospheric conditions and a 30° solar zenith angle. From DeMore, W. B., et al. *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*. JPL Publication 97-4. Pasadena, Calif.: Jet Propulsion Lab, 1997.

"Introduction to Atmospheric Chemistry," D. J. Jacob, Princeton Univ. Press, Princeton, (1999).

CFC (クロロフルオロカーボン)

1961 Lovelock – ECD 開発

ハロゲン・硫黄を含む化合物の高感度検出器
[Anal. Chem., 33, 162 (1961)]



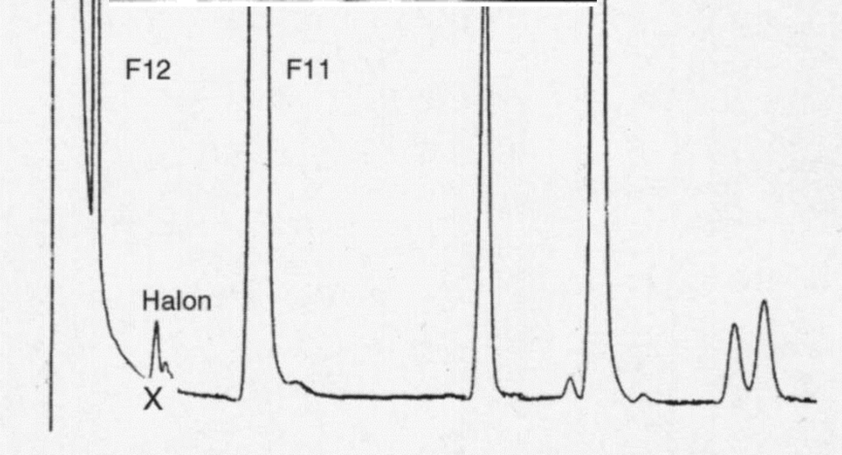
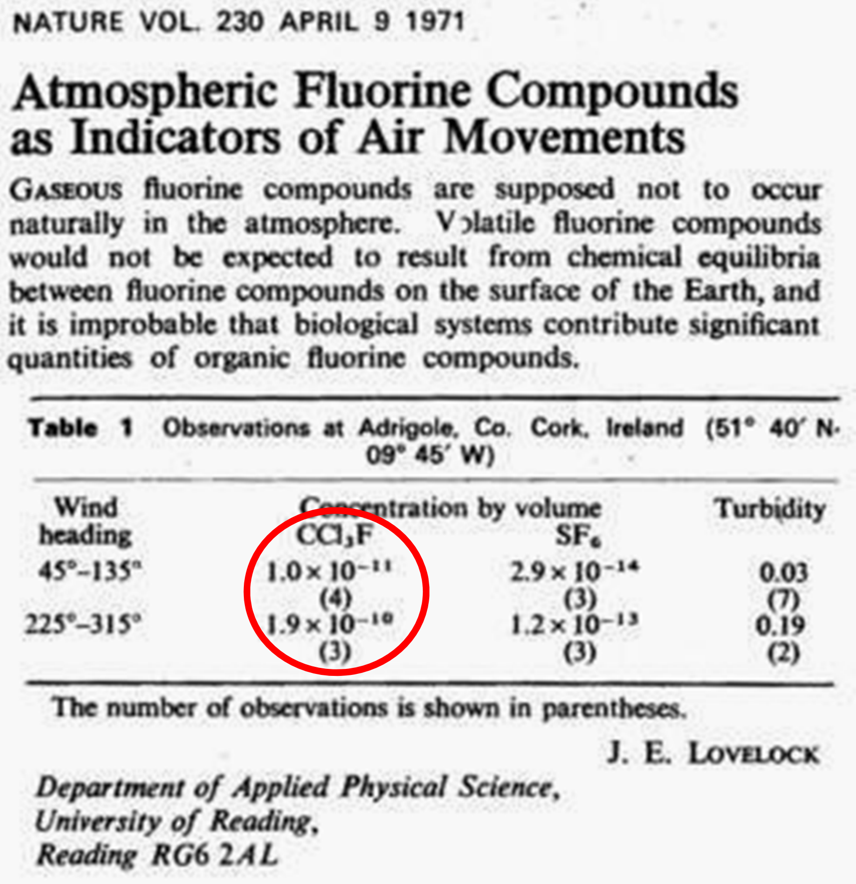


Figure 1. A chromatogram to illustrate the sensitivity of the ECD. The peak ‘X’ represents 1.1 parts per trillion of Halon in the air

J. Lovelock, "Homage to Gaia," Oxford Univ. Press, Oxford (2000).

1971 Lovelock – 大気中 CFC-11

天然には存在しない CCl_3F を大気中で測定
[Nature, 230, 379 (1971)]



NATURE VOL. 230 APRIL 9 1971

Atmospheric Fluorine Compounds as Indicators of Air Movements

GASEOUS fluorine compounds are supposed not to occur naturally in the atmosphere. Volatile fluorine compounds would not be expected to result from chemical equilibria between fluorine compounds on the surface of the Earth, and it is improbable that biological systems contribute significant quantities of organic fluorine compounds.

Table 1 Observations at Adrigole, Co. Cork, Ireland (51° 40′ N-09° 45′ W)

Wind heading	Concentration by volume CCl_3F	SF_6	Turbidity
45°–135°	1.0×10^{-11} (4)	2.9×10^{-14} (3)	0.03 (7)
225°–315°	1.9×10^{-10} (3)	1.2×10^{-13} (3)	0.19 (2)

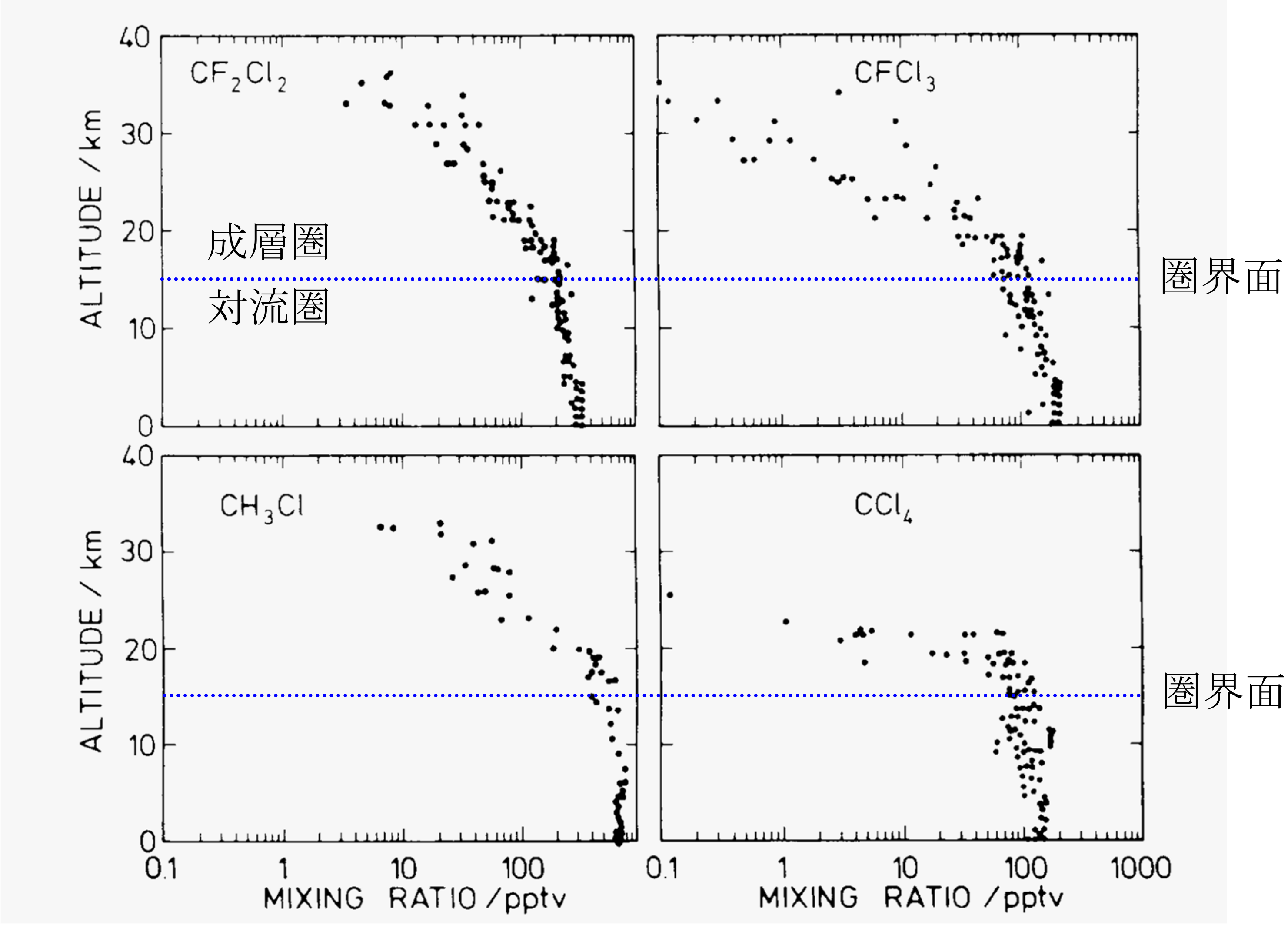
The number of observations is shown in parentheses.

J. E. LOVELOCK

Department of Applied Physical Science,
University of Reading,
Reading RG6 2AL

大気中の CFC (クロロフルオロカーボン)

大気中 CFC の鉛直分布



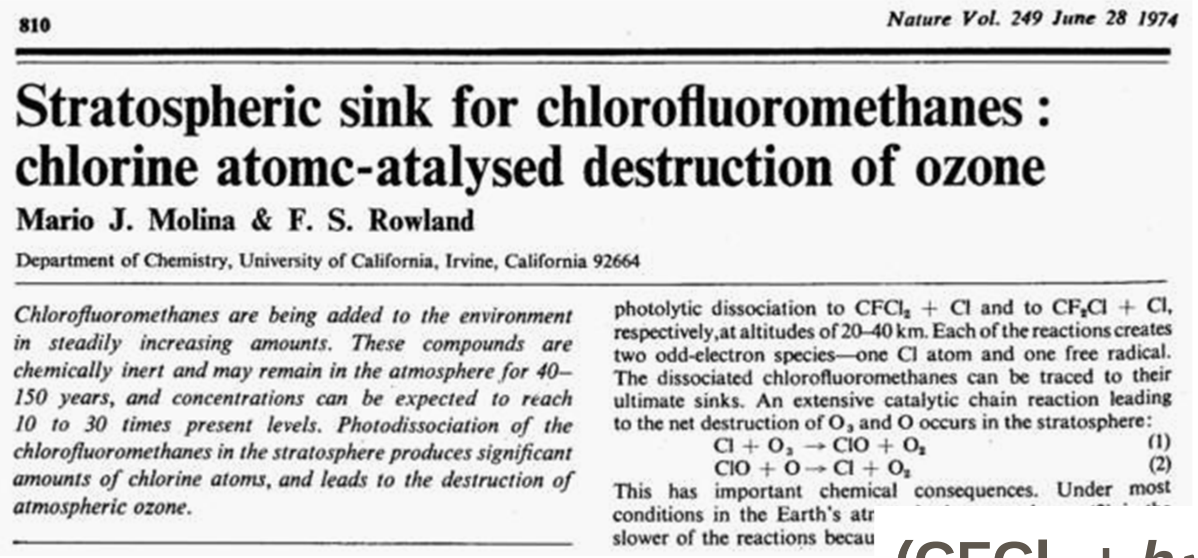
圏界面 (~15 km) で急激な減少 → <u>成層圏で分解</u>

"Chemistry of the Natural Atmosphere," P. Warneck, Academic Press, San Diego (1988).

オゾン層

1974 Molina & Rowland – オゾン層破壊予言

[Nature, 249, 810 (1974)] (1995ノーベル化学賞)



810 Nature Vol. 249 June 28 1974

Stratospheric sink for chlorofluoromethanes : chlorine atomc-atalysed destruction of ozone

Mario J. Molina & F. S. Rowland

Department of Chemistry, University of California, Irvine, California 92664

Chlorofluoromethanes are being added to the environment in steadily increasing amounts. These compounds are chemically inert and may remain in the atmosphere for 40–150 years, and concentrations can be expected to reach 10 to 30 times present levels. Photodissociation of the chlorofluoromethanes in the stratosphere produces significant amounts of chlorine atoms, and leads to the destruction of atmospheric ozone.

photolytic dissociation to $CFCl_2$ + Cl and to CF_2Cl + Cl, respectively, at altitudes of 20–40 km. Each of the reactions creates two odd-electron species—one Cl atom and one free radical. The dissociated chlorofluoromethanes can be traced to their ultimate sinks. An extensive catalytic chain reaction leading to the net destruction of O_3 and O occurs in the stratosphere:

$$Cl + O_3 \rightarrow ClO + O_2 \quad (1)$$

$$ClO + O \rightarrow Cl + O_2 \quad (2)$$

This has important chemical consequences. Under most conditions in the Earth's atr

slower of the reactions becau

$$(CFCl_3 + h\nu \rightarrow CFCl_2 + Cl)$$

連鎖反応

$$Cl + O_3 \rightarrow ClO + O_2$$

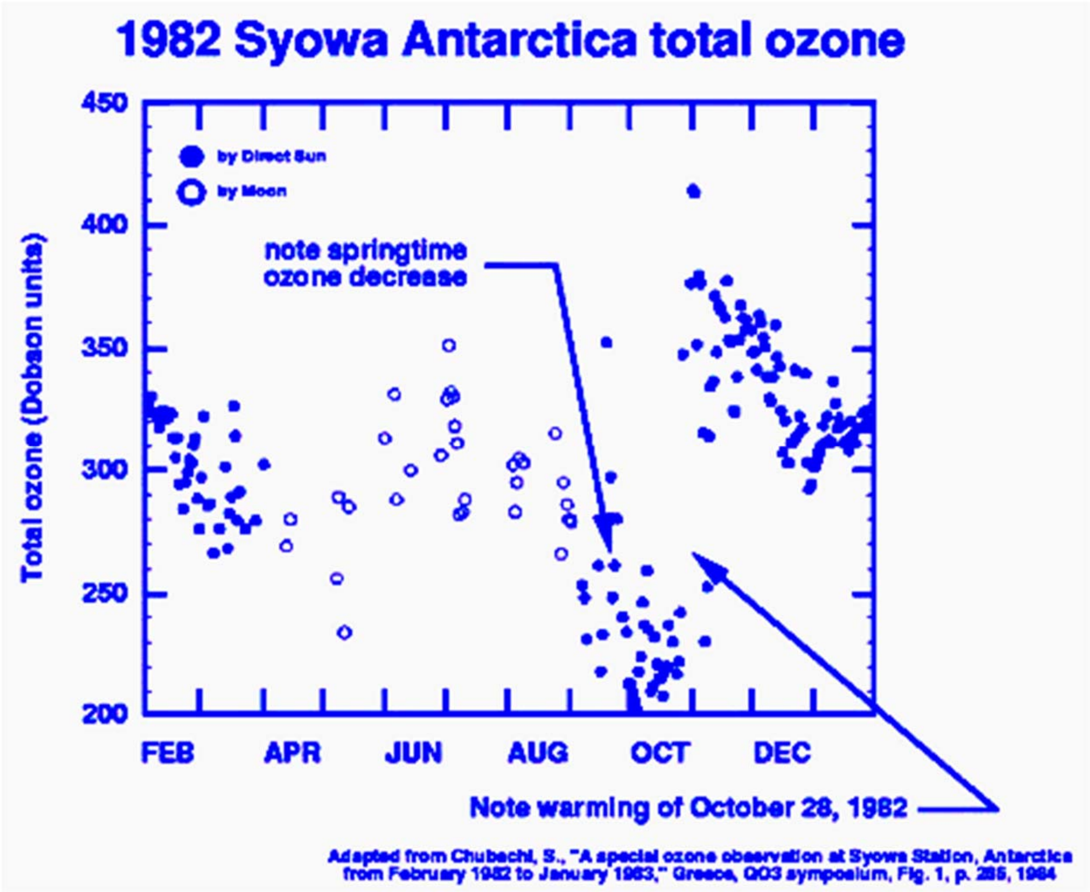
$$ClO + O \rightarrow Cl + O_2$$

$$\text{net: } O_3 + O \rightarrow 2\,O_2$$

1 つの Cl 原子が ~10^4 個
のオゾン (O_3) を破壊

昭和基地上空のオゾン

1984 Chubachi – 南極オゾン異常減少 (1982)



Adapted from Chubachi, S., "A special ozone observation at Syowa Station, Antarctica from February 1982 to January 1983," Greece, QO3 symposium, Fig. 1, p. 285, 1984

cf.) 100 DU
= 1mm O_3 STP

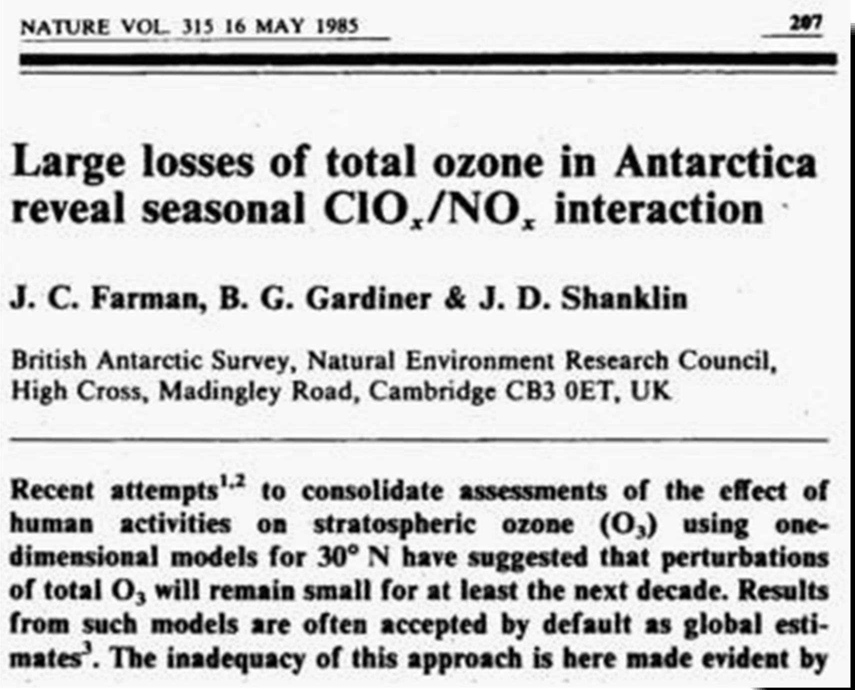
S. Chubachi,"A special ozone observation at Syowa Station, Antarctica from February 1982 to January 1983," Greece, QO3 symposium, Fig. 1, p. 286, 1984

南極オゾンホール

≠ オゾン層破壊

1985 Farman et al. – 南極オゾンホール

[Nature, 315, 207 (1985)]



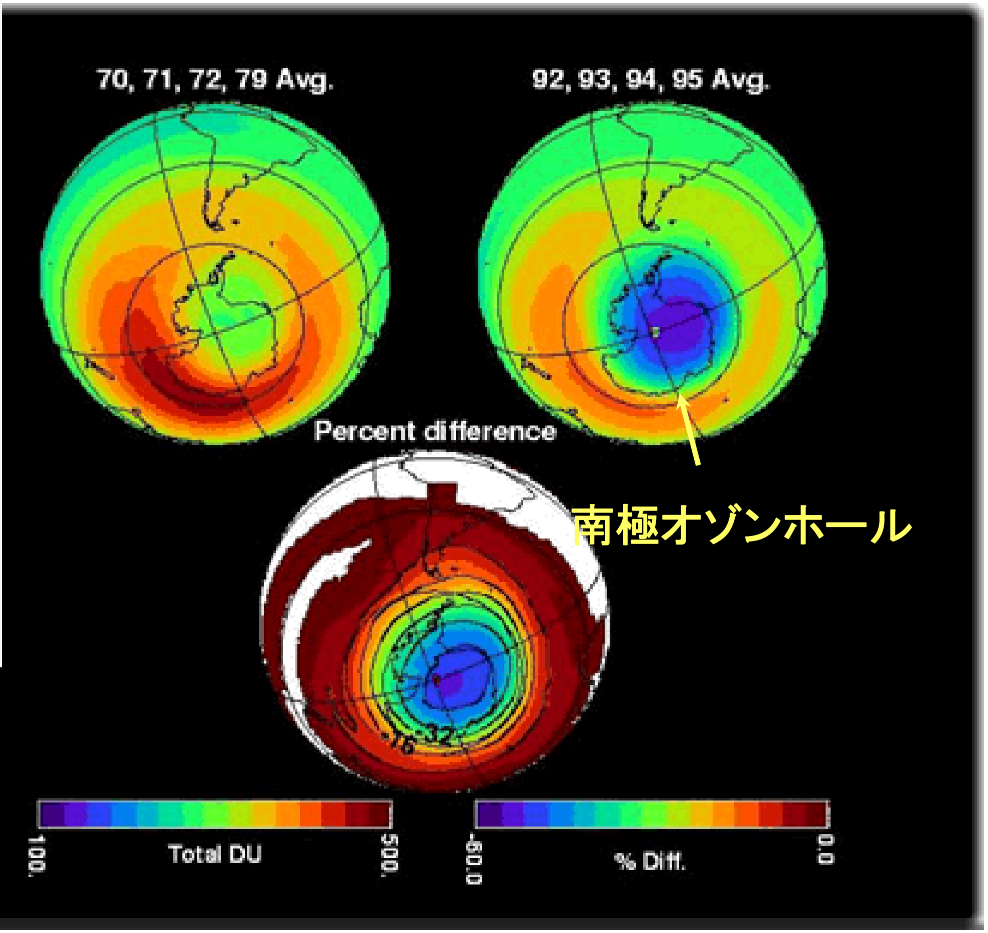
NATURE VOL. 315 16 MAY 1985 207

Large losses of total ozone in Antarctica reveal seasonal ClO_x/NO_x interaction

J. C. Farman, B. G. Gardiner & J. D. Shanklin

British Antarctic Survey, Natural Environment Research Council,
High Cross, Madingley Road, Cambridge CB3 0ET, UK

Recent attempts[1,2] to consolidate assessments of the effect of human activities on stratospheric ozone (O_3) using one-dimensional models for 30° N have suggested that perturbations of total O_3 will remain small for at least the next decade. Results from such models are often accepted by default as global estimates[3]. The inadequacy of this approach is here made evident by

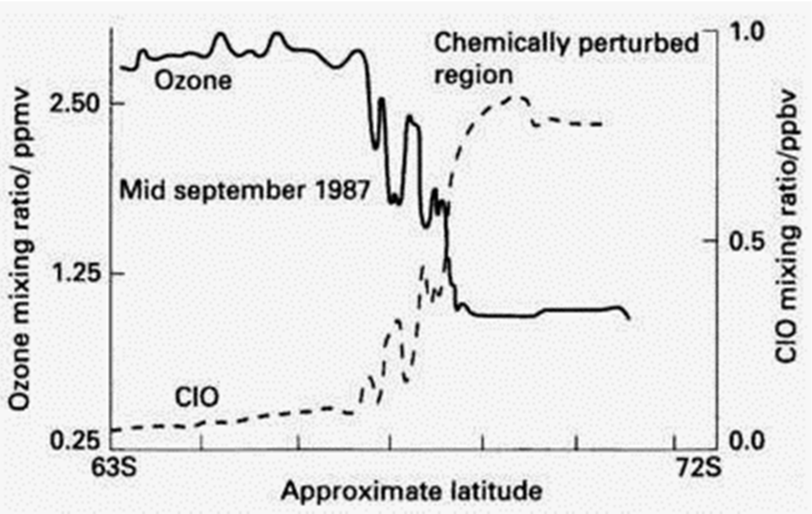


南極オゾンホール

http://www.ccpo.odu.edu/SEES/index.html

南極オゾンホールと CFC

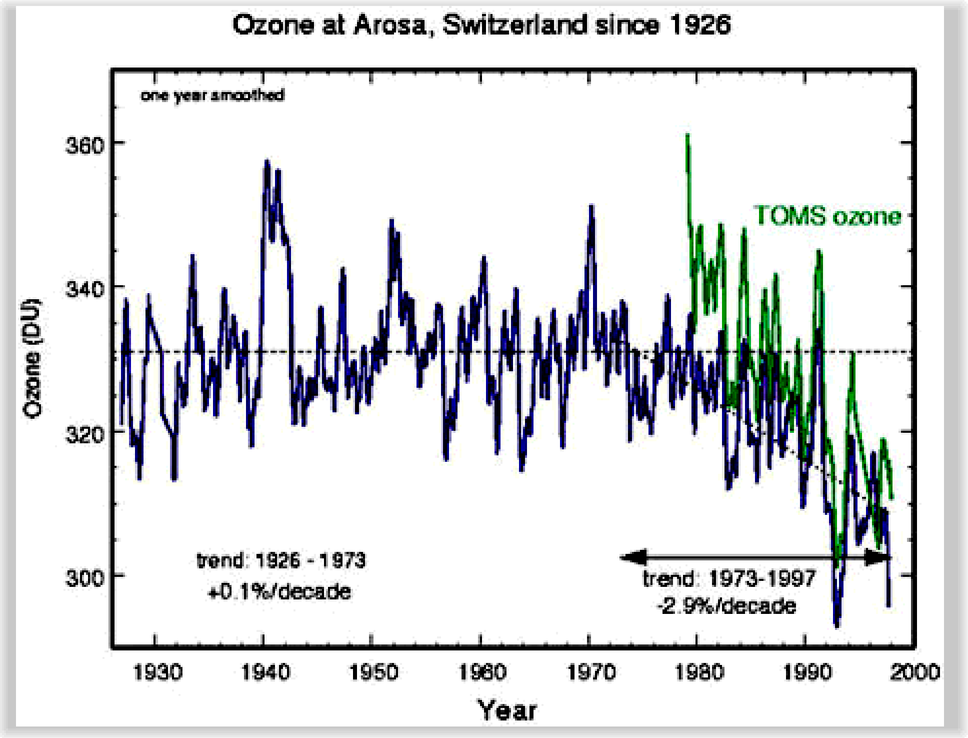
1985 オゾン層保護条約
1987 モントリオール議定書



南極オゾンホール端での ClO, O_3 濃度

"Reaction Kinetics," M. J. Pilling and P. W. Seakins, Oxford Univ. Press, Oxford (1995).

中緯度成層圏オゾンの減少

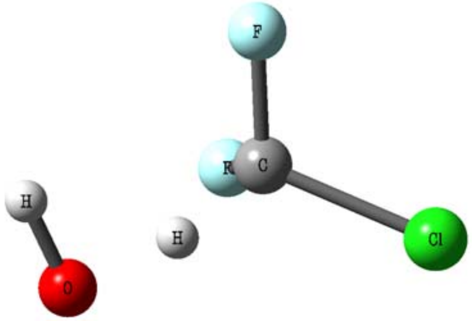


http://www.ccpo.odu.edu/SEES/index.html

CFC 代替技術

DuPont 社 - CFC代替品開発

量子化学計算によるスクリーニング
Gaussian (J. A. Pople 1998 ノーベル化学賞)



cf.) HCFC-22 と OH ラジカルの反応の遷移状態

対流圏(大気中)寿命

CFC, 代替品 (HCFC/HFC)	k_{OH} / cm^3 molecule^{-1} s^{-1}	τ_{OH} / yr	ODP	GWP (100yr)
冷媒用				
CFC-12 (CCl_2F_2)	–	**102**	**1**	**8500**
HCFC-22 ($CHClF_2$)	4.6×10^{-15}	**13.3**	**0.055**	**1700**
HFC-134a (CH_2FCF_3)	4.2×10^{-15}	15	0	1300
発泡用				
CFC-11 (CCl_3F)	–	**50**	**1**	**4000**
HCFC-141b (CH_3CCl_2F)	5.9×10^{-15}	**9.4**	**0.11**	**630**
HCFC-142b (CH_3CClF_2)	3.0×10^{-15}	19.5	0.065	2000

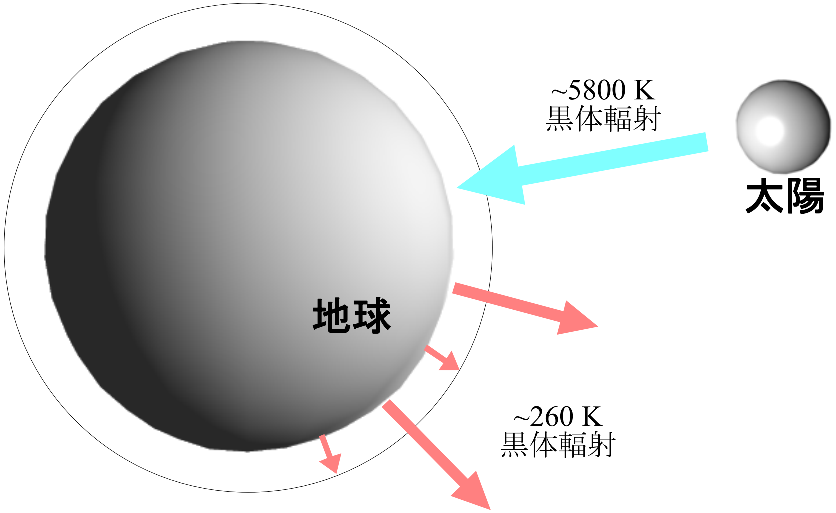
$$\tau_{OH} = 1 / ([OH]_{ss} \times k_{OH})$$

$[OH]_{ss} \sim 5\times10^5$ molecules cm^{-3}

気候変動

Climate Change

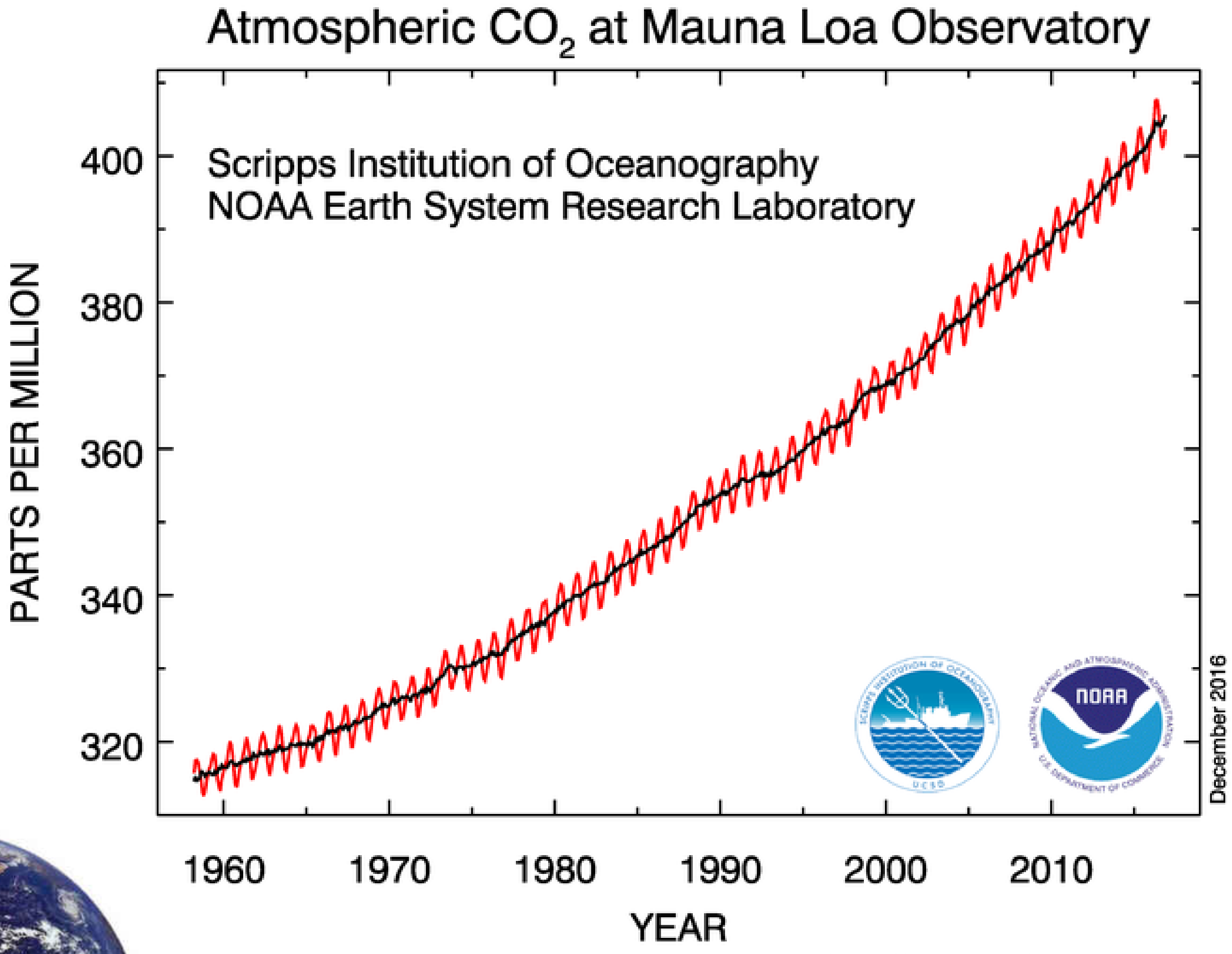
地球 = 巨大システム



継続観測による事実

事実としての CO$_2$ 濃度
(~60年前から)

1958– C. D. Keeling & co-workers
Mauna Loa Observatory (Hawaii) – 大気観測


Atmospheric CO$_2$ at Mauna Loa Observatory

http://www.esrl.noaa.gov/gmd/ccgg/trends/

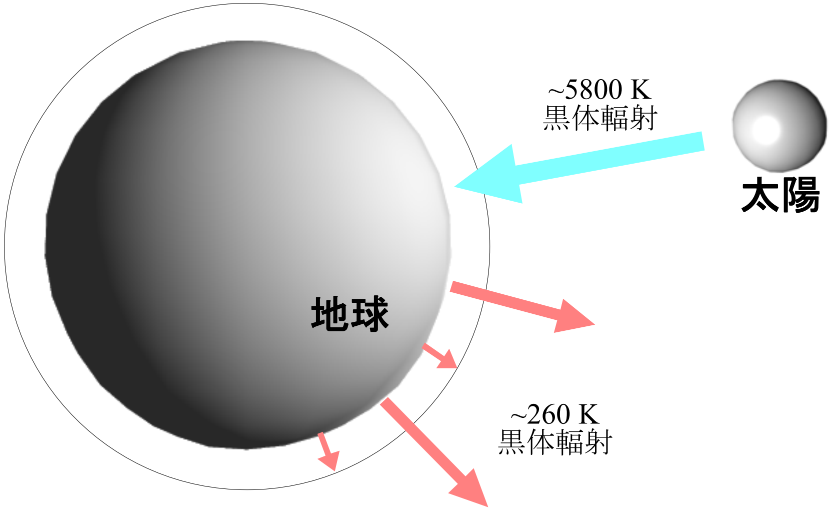
温室効果

原理: 19世紀
(~120年前)

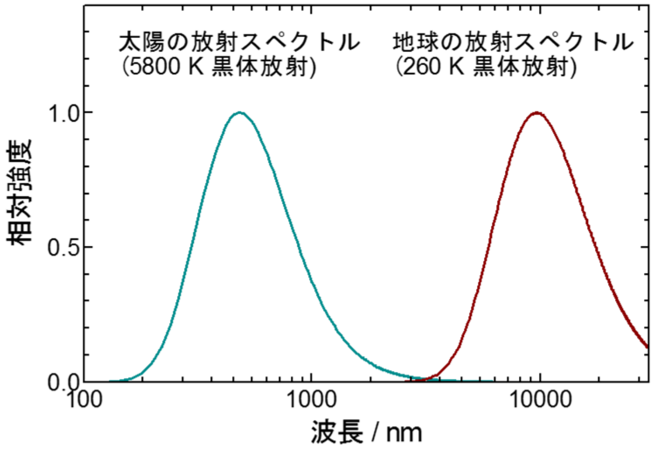
19世紀 Svante Arrhenius – CO_2 による温室効果

– “On the Influence of Carbonic Acid in the Air upon the Temperature of the Ground”
[Philosophical Magazine 41, 237 (1896)]

> A great deal has been written on the influence of the absorption of the atmosphere upon the climate. Tyndall [2] in particular has pointed out the enormous importance of this question. To him it was chiefly the diurnal and annual variation of the temperature that were lessened by this circumstance. Another side of the question, that has long attracted the attention of physicists, is this: Is the mean temperature of the ground in any way influenced by the presence of heat-absorbing gases in the atmosphere? Fourier [3] maintained that the atmosphere acts like the glass of a hot-house, because it lets through the light rays of the sun but retains the dark rays from the ground. This idea was elaborated by Pouillet [4]; and Langley was by some of his researches led to the view, that "the temperature of the earth under direct sunshine, even though our atmosphere were present as now, would probably fall to –200 ° C., if that atmosphere did not possess the quality of selective absorption“ [5]. This view, which was founded on too wide a use of Newton's law of cooling, must be abandoned, as Langley himself in a later memoir showed that the full moon, which certainly does not posses any sensible heat-absorbing atmosphere, has a "mean effective temperature" of about 45 ° C. [6]

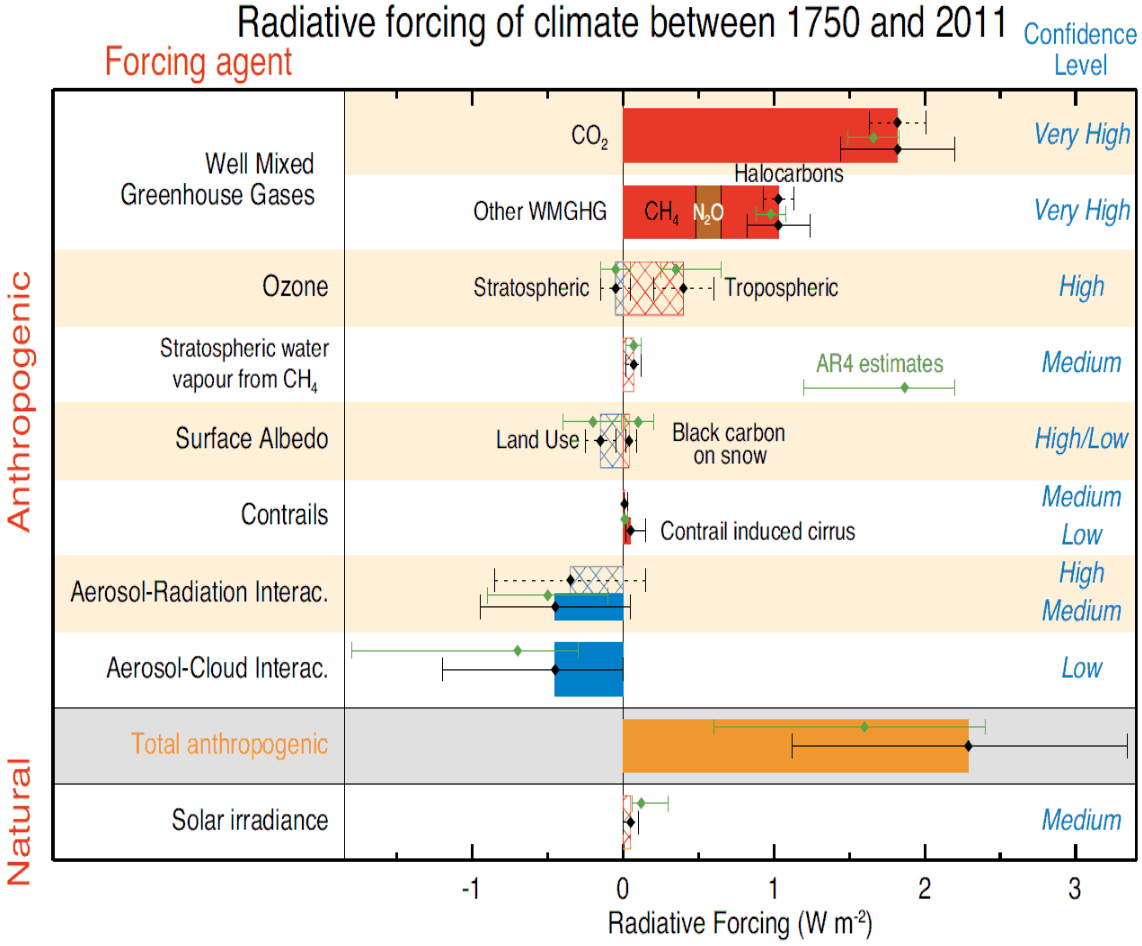


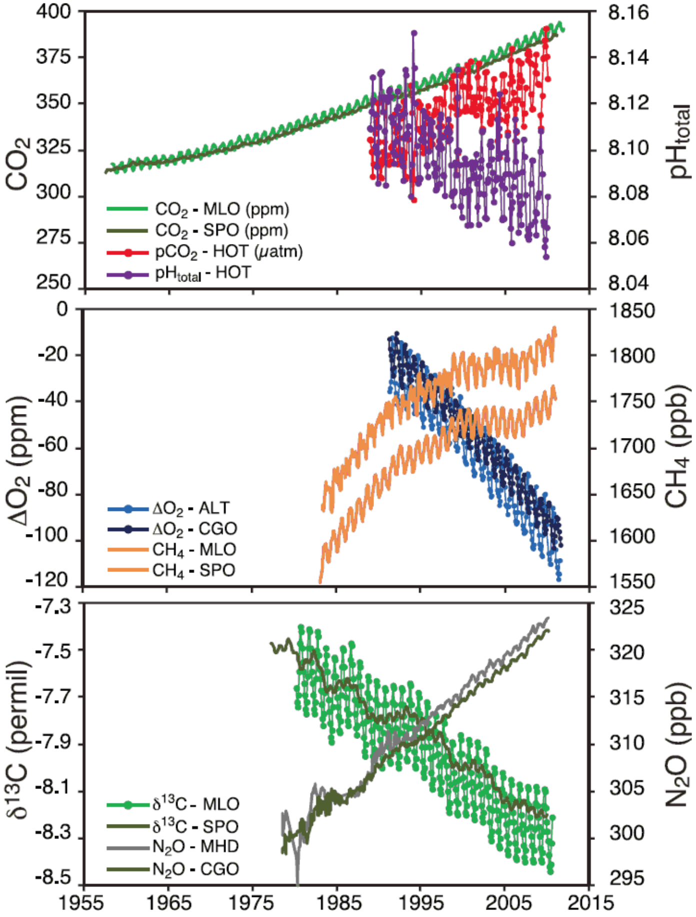
収支に関わる波長の違い



放射強制力への様々な寄与

増加を続ける CO_2(二酸化炭素), CH_4(メタン), N_2O(亜酸化窒素)





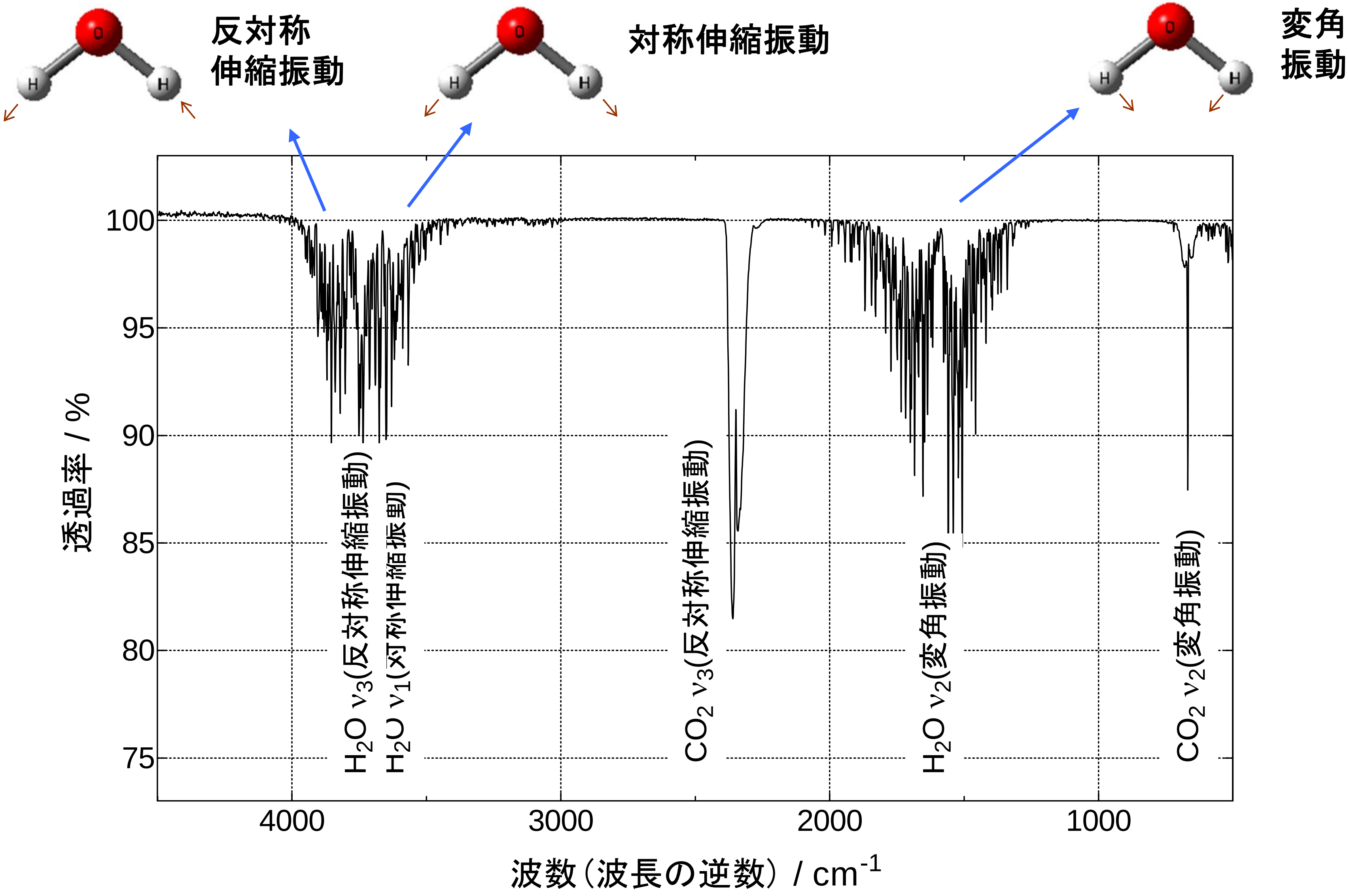
放射強制力への多用な寄与

Climate Change 2013 - The Physical Science Basis
Working Group I Contribution to the Fifth Assessment Report of the IPCC
available at http://www.ipcc.ch/

温室効果気体

大気の赤外吸収スペクトル　(光路長 10 cm)

分子の振動と回転に起因する複雑なスペクトル



反対称伸縮振動

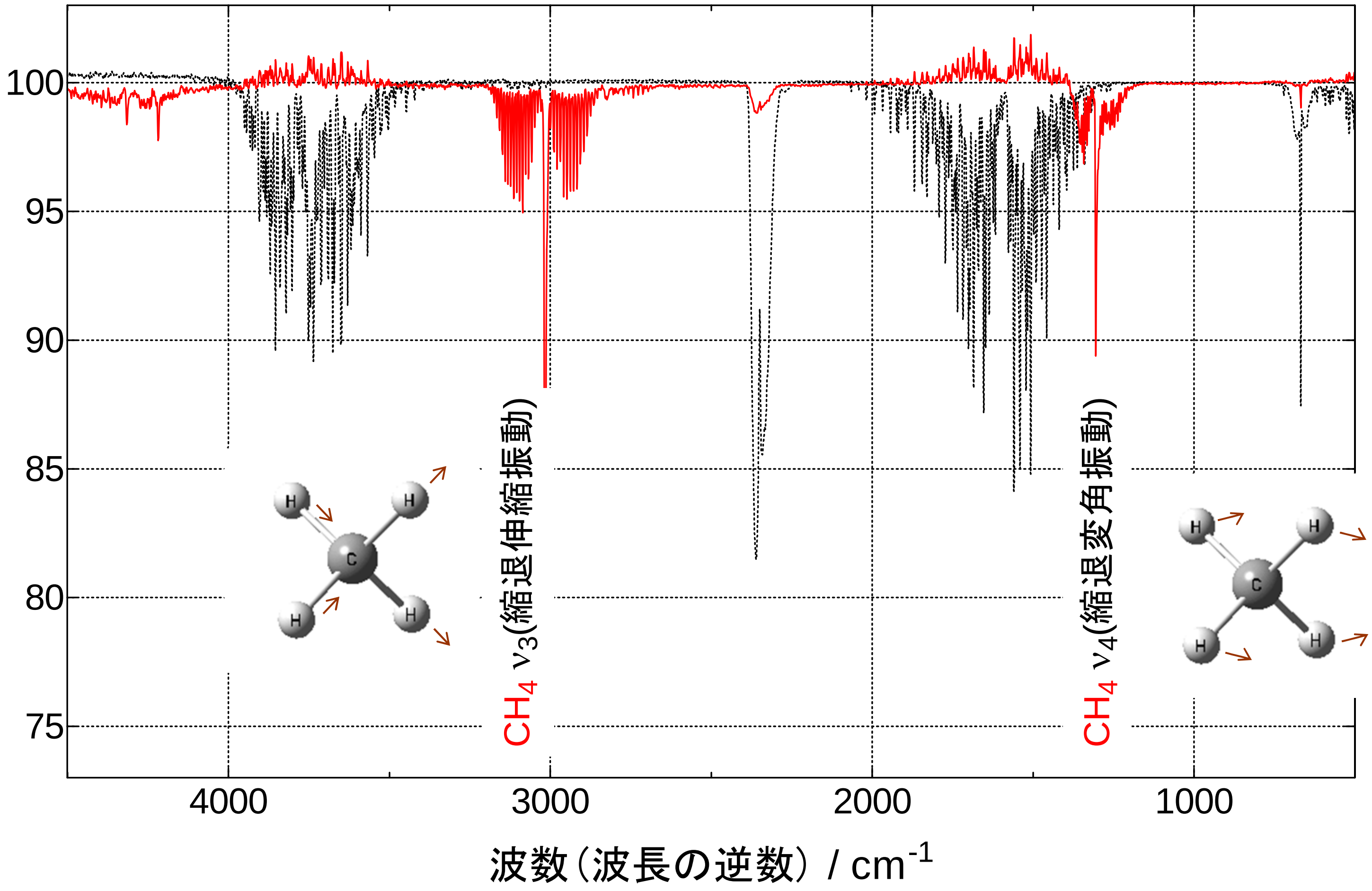
対称伸縮振動

変角振動

メタン – 温室効果気体

H_2O, CO_2の吸収のない
大気の「窓」に吸収をもつ → 温室効果大

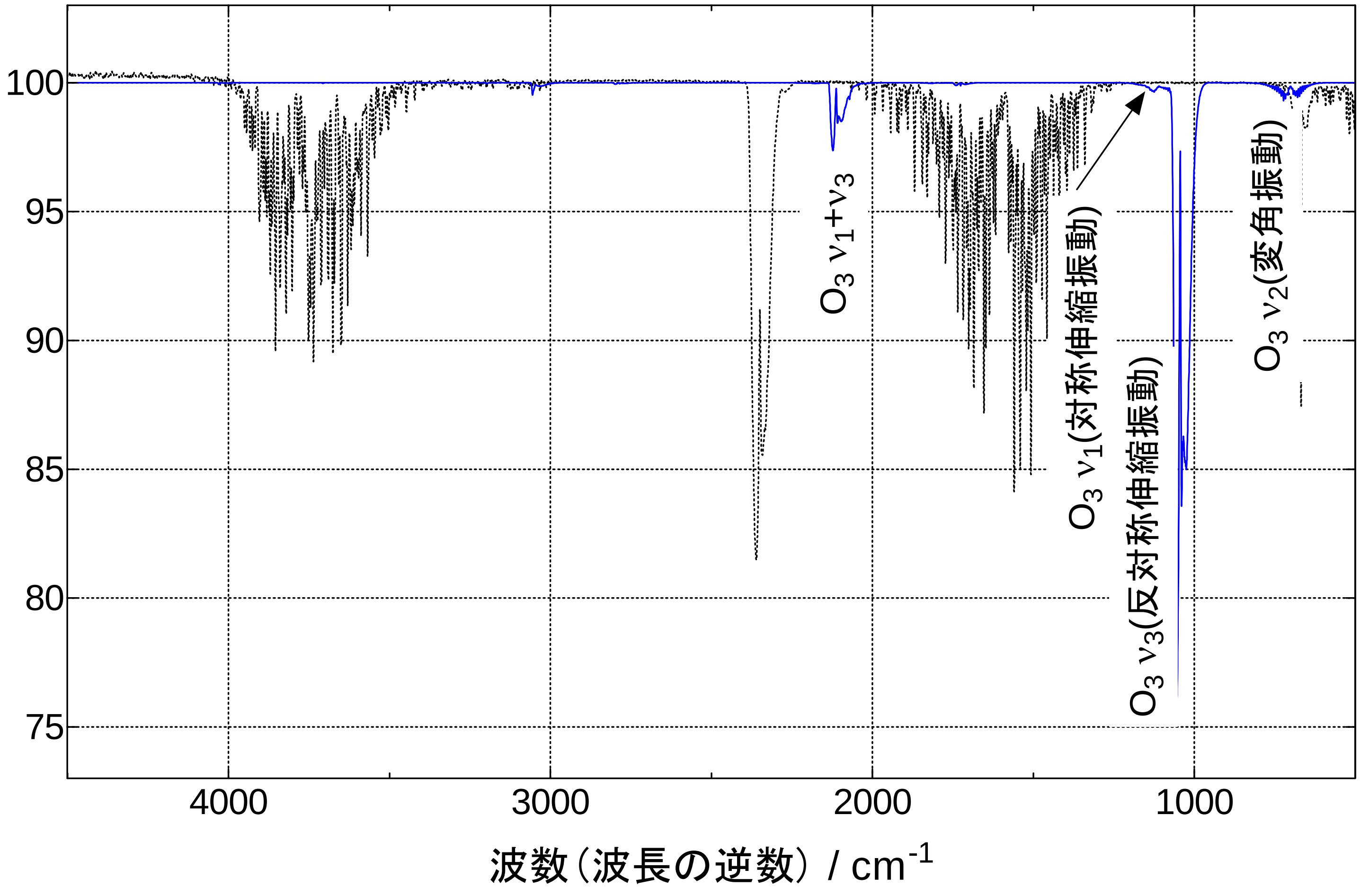
メタン・大気の赤外吸収スペクトル



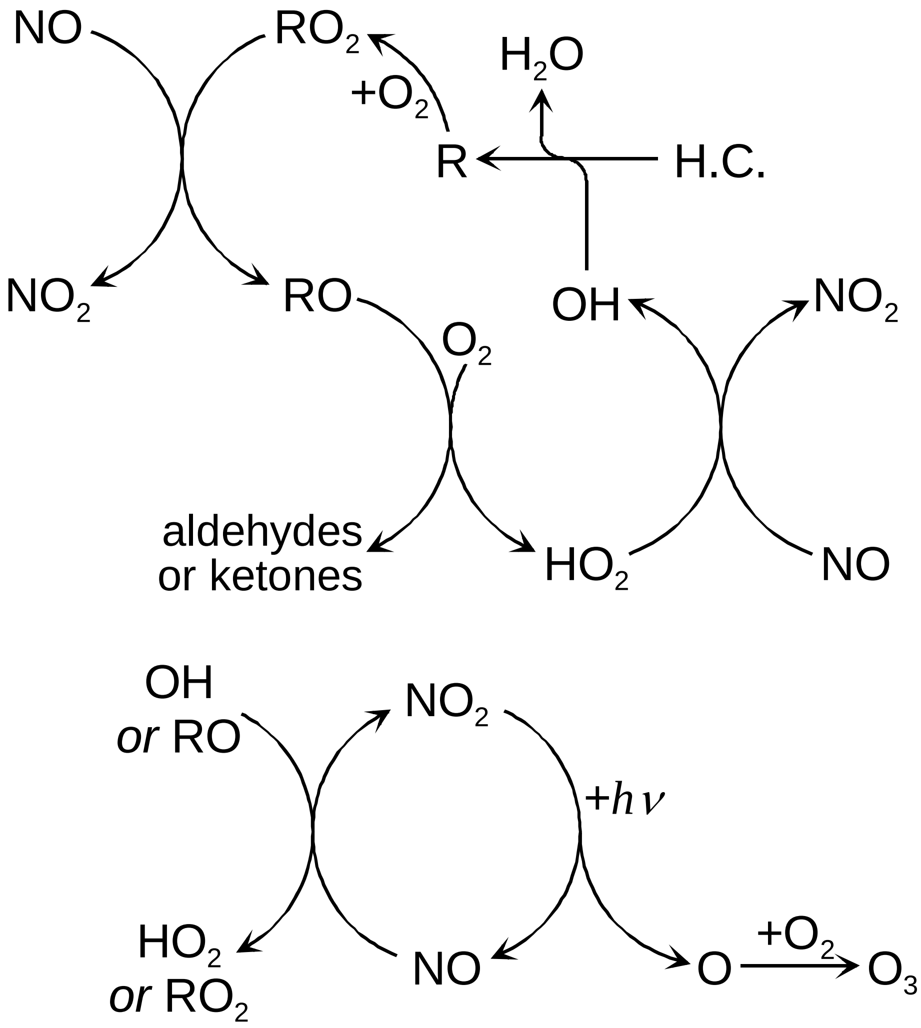
オゾン – 温室効果気体

成層圏のオゾン … ○ 紫外線を遮蔽
対流圏のオゾン … × 温室効果気体

オゾン・大気の赤外吸収スペクトル



対流圏のオゾン



HC(炭化水素) / NO$_x$ ← 大気汚染

光化学スモッグ
O_3 (オキシダントの主成分)

HC 酸化 ... XO_2 (HO_2/RO_2)

$NO + XO_2 \rightarrow NO_2 + XO$

$NO_2 + h\nu \rightarrow O + NO$

$O + O_2 + M \rightarrow O_3 + M$

$O_3 + h\nu \rightarrow O(^1D) + O_2$

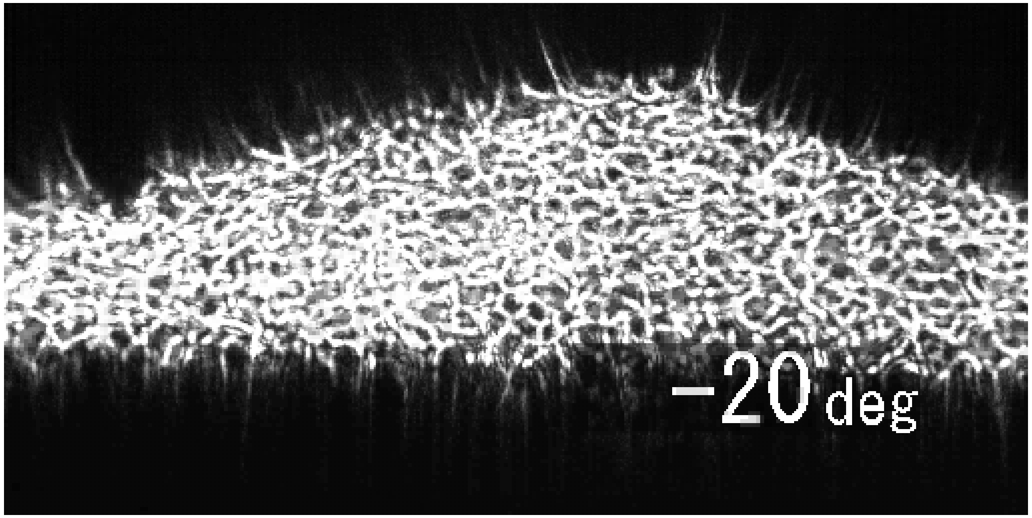
$O(^1D) + H_2O \rightarrow$ **OH + OH**

OH ラジカル
(大気の掃除屋/洗浄剤)
の発生源 (detergent of the atmosphere)

自然起源 NO$_x$ ← 土壌/雷

燃焼技術

combustion technology



ガソリンエンジン
内の可視化映像

by courtesy of
Dr. M. Kaneko

SUBARU

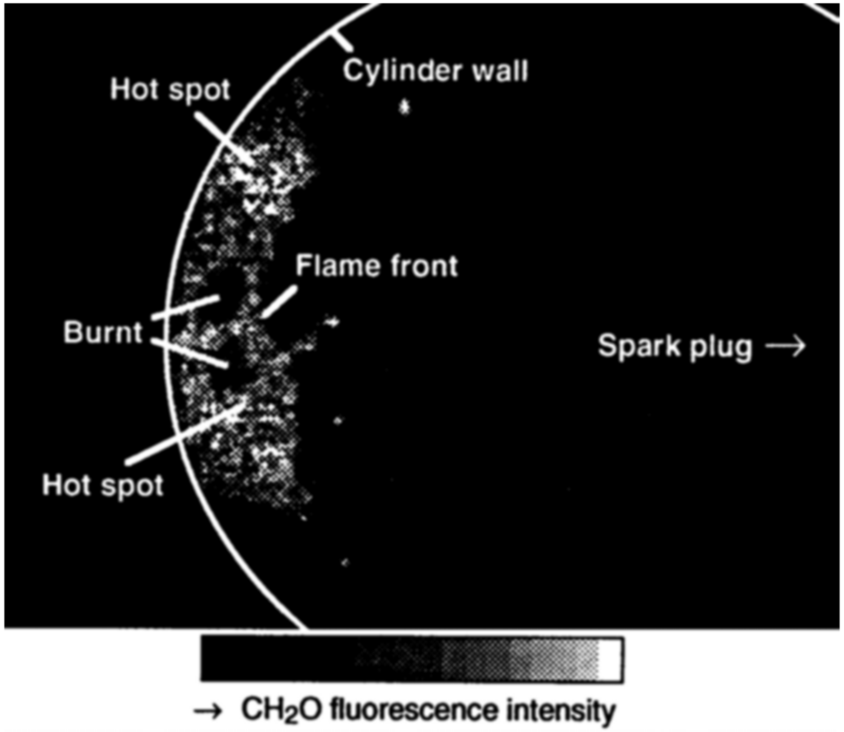
エンジンノック — 課題

— 現象

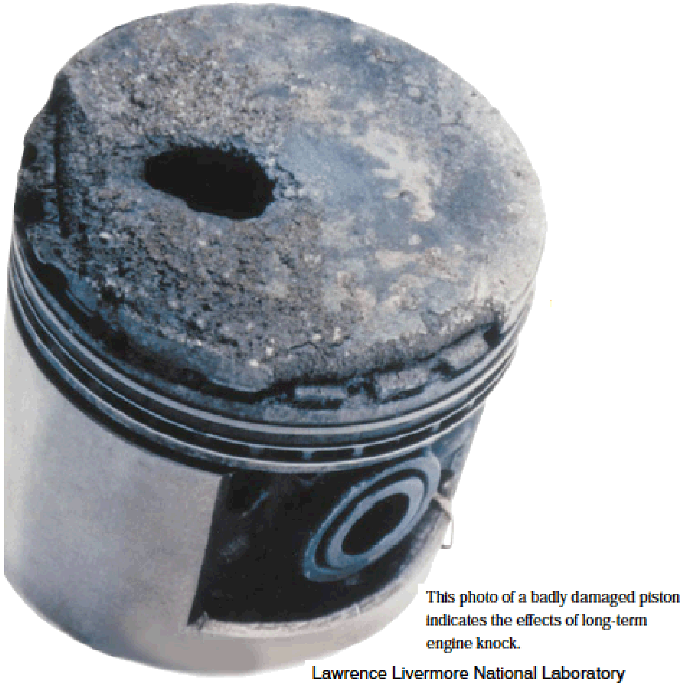
- 自動車エンジンで発生する好ましくない自着火

— 問題

- 機関の致命的損傷
- 抑制 (低圧縮比化/着火時期遅延) は 熱効率の低下 を伴う



J. Warnatz, U. Maas, and R. W. Dibble, "Combustion," Springer, Berlin, 1996.



This photo of a badly damaged piston indicates the effects of long-term engine knock.

Lawrence Livermore National Laboratory

Science and Technology Review, Dec. 1999, Lawrence Livermore National Laboratory, UCRL-52000-99012 (1999).

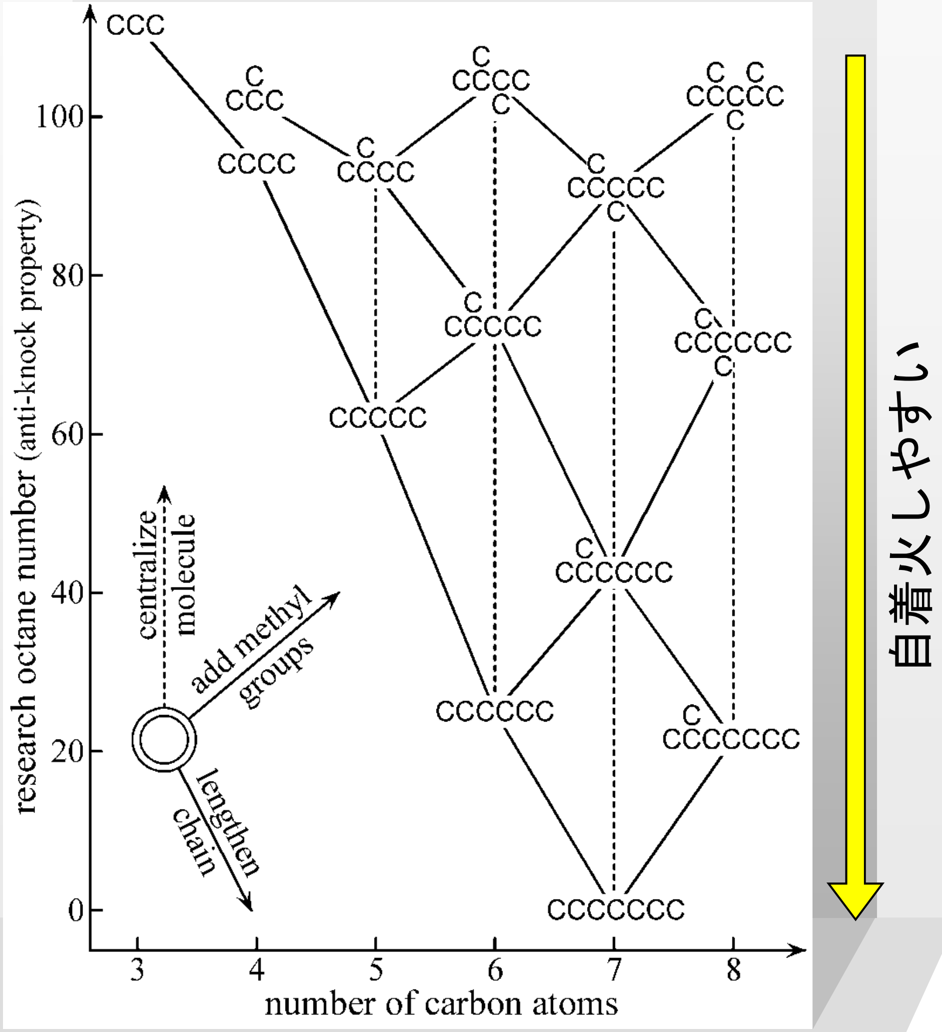
オクタン価

– ガソリンの耐ノック性の指標

- オクタン価が高い
  = 自着火しにくい
  (良質なガソリン)
- 燃料炭化水素の化学構造と明瞭な関係がある

→ **どうしてか？**

→ **どう** 制御するのか**？**



based on: W. G. Lovell, *Ind. Eng. Chem.*, 40, 2388 (1948).

燃焼の化学反応

- 膨大な数の化学反応
  - 気相の均一相燃焼でも

    H_2 の燃焼機構：

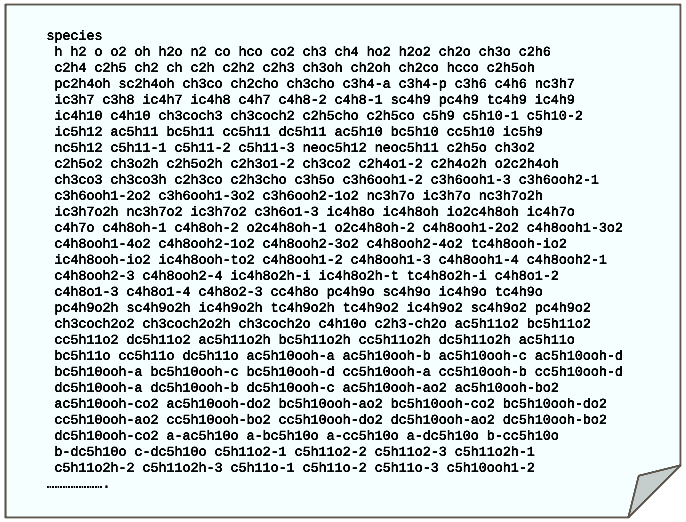
    8 化学種 20 素反応

    n-ヘプタン (C_7H_{16}) の燃焼：

    ~540 化学種 **~2450** 素反応

    i-オクタン (C_8H_{18}) の燃焼：

    ~850 化学種 **~3600** 素反応



```
species
 h h2 o o2 oh h2o n2 co hco co2 ch3 ch4 ho2 h2o2 ch2o ch3o c2h6
 c2h4 c2h5 ch2 ch c2h c2h2 c2h3 ch3oh ch2oh ch2co hcco c2h5oh
 pc2h4oh sc2h4oh ch3co ch2cho ch3cho c3h4-a c3h4-p c3h6 c4h6 nc3h7
 ic3h7 c3h8 ic4h7 ic4h8 c4h7 c4h8-2 c4h8-1 sc4h9 pc4h9 tc4h9 ic4h9
 ic4h10 c4h10 ch3coch3 ch3coch2 c2h5cho c2h5co c5h9 c5h10-1 c5h10-2
 ic5h12 ac5h11 bc5h11 cc5h11 dc5h11 ac5h10 bc5h10 cc5h10 ic5h9
 nc5h12 c5h11-1 c5h11-2 c5h11-3 neoc5h12 neoc5h11 c2h5o ch3o2
 c2h5o2 ch3o2h c2h5o2h c2h3o1-2 ch3co2 c2h4o1-2 c2h4o2h o2c2h4oh
 ch3co3 ch3co3h c2h3co c2h3cho c3h5o c3h6ooh1-2 c3h6ooh1-3 c3h6ooh2-1
 c3h6ooh1-2o2 c3h6ooh1-3o2 c3h6ooh2-1o2 nc3h7o ic3h7o nc3h7o2h
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 c4h7o c4h8oh-1 c4h8oh-2 o2c4h8oh-1 o2c4h8oh-2 c4h8ooh1-2o2 c4h8ooh1-3o2
 c4h8ooh1-4o2 c4h8ooh2-1o2 c4h8ooh2-3o2 c4h8ooh2-4o2 tc4h8ooh-io2
 ic4h8ooh-io2 ic4h8ooh-to2 c4h8ooh1-2 c4h8ooh1-3 c4h8ooh1-4 c4h8ooh2-1
 c4h8ooh2-3 c4h8ooh2-4 ic4h8o2h-i ic4h8o2h-t tc4h8o2h-i c4h8o1-2
 c4h8o1-3 c4h8o1-4 c4h8o2-3 cc4h8o pc4h9o sc4h9o ic4h9o tc4h9o
 pc4h9o2h sc4h9o2h ic4h9o2h tc4h9o2h tc4h9o2 ic4h9o2 sc4h9o2 pc4h9o2
 ch3coch2o2 ch3coch2o2h ch3coch2o c4h10o c2h3-ch2o ac5h11o2 bc5h11o2
 cc5h11o2 dc5h11o2 ac5h11o2h bc5h11o2h cc5h11o2h dc5h11o2h ac5h11o
 bc5h11o cc5h11o dc5h11o ac5h10ooh-a ac5h10ooh-b ac5h10ooh-c ac5h10ooh-d
 bc5h10ooh-a bc5h10ooh-c bc5h10ooh-d cc5h10ooh-a cc5h10ooh-b cc5h10ooh-d
 dc5h10ooh-a dc5h10ooh-b dc5h10ooh-c ac5h10ooh-ao2 ac5h10ooh-bo2
 ac5h10ooh-co2 ac5h10ooh-do2 bc5h10ooh-ao2 bc5h10ooh-co2 bc5h10ooh-do2
 cc5h10ooh-ao2 cc5h10ooh-bo2 cc5h10ooh-do2 dc5h10ooh-ao2 dc5h10ooh-bo2
 dc5h10ooh-co2 a-ac5h10o a-bc5h10o a-cc5h10o a-dc5h10o b-cc5h10o
 b-dc5h10o c-dc5h10o c5h11o2-1 c5h11o2-2 c5h11o2-3 c5h11o2h-1
 c5h11o2h-2 c5h11o2h-3 c5h11o-1 c5h11o-2 c5h11o-3 c5h10ooh1-2
…………………….
```
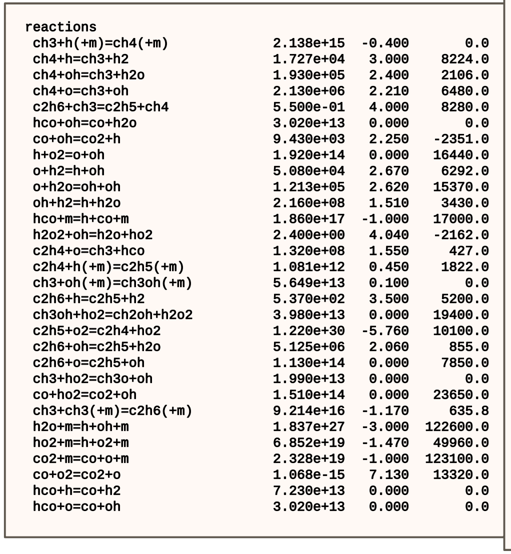
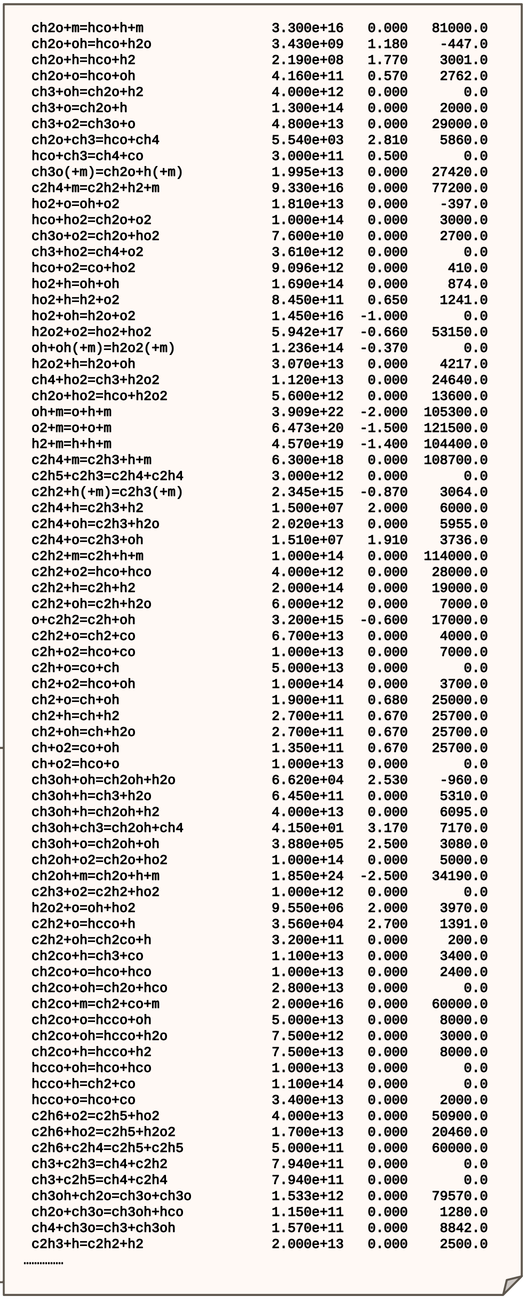



```
reactions
 ch3+h(+m)=ch4(+m)                2.138e+15  -0.400       0.0
 ch4+h=ch3+h2                     1.727e+04   3.000    8224.0
 ch4+oh=ch3+h2o                   1.930e+05   2.400    2106.0
 ch4+o=ch3+oh                     2.130e+06   2.210    6480.0
 c2h6+ch3=c2h5+ch4                5.500e-01   4.000    8280.0
 hco+oh=co+h2o                    3.020e+13   0.000       0.0
 co+oh=co2+h                      9.430e+03   2.250   -2351.0
 h+o2=o+oh                        1.920e+14   0.000   16440.0
 o+h2=h+oh                        5.080e+04   2.670    6292.0
 o+h2o=oh+oh                      1.213e+05   2.620   15370.0
 oh+h2=h+h2o                      2.160e+08   1.510    3430.0
 hco+m=h+co+m                     1.860e+17  -1.000   17000.0
 h2o2+oh=h2o+ho2                  2.400e+00   4.040   -2162.0
 c2h4+o=ch3+hco                   1.320e+08   1.550     427.0
 c2h4+h(+m)=c2h5(+m)              1.081e+12   0.450    1822.0
 ch3+oh(+m)=ch3oh(+m)             5.649e+13   0.100       0.0
 c2h6+h=c2h5+h2                   5.370e+02   3.500    5200.0
 ch3oh+ho2=ch2oh+h2o2             3.980e+13   0.000   19400.0
 c2h5+o2=c2h4+ho2                 1.220e+30  -5.760   10100.0
 c2h6+oh=c2h5+h2o                 5.125e+06   2.060     855.0
 c2h6+o=c2h5+oh                   1.130e+14   0.000    7850.0
 ch3+ho2=ch3o+oh                  1.990e+13   0.000       0.0
 co+ho2=co2+oh                    1.510e+14   0.000   23650.0
 ch3+ch3(+m)=c2h6(+m)             9.214e+16  -1.170     635.8
 h2o+m=h+oh+m                     1.837e+27  -3.000  122600.0
 ho2+m=h+o2+m                     6.852e+19  -1.470   49960.0
 co2+m=co+o+m                     2.328e+19  -1.000  123100.0
 co+o2=co2+o                      1.068e-15   7.130   13320.0
 hco+h=co+h2                      7.230e+13   0.000       0.0
 hco+o=co+oh                      3.020e+13   0.000       0.0
```



```
 ch2o+m=hco+h+m                   3.300e+16   0.000   81000.0
 ch2o+oh=hco+h2o                  3.430e+09   1.180    -447.0
 ch2o+h=hco+h2                    2.190e+08   1.770    3001.0
 ch2o+o=hco+oh                    4.160e+11   0.570    2762.0
 ch3+oh=ch2o+h2                   4.000e+12   0.000       0.0
 ch3+o=ch2o+h                     1.300e+14   0.000    2000.0
 ch3+o2=ch3o+o                    4.800e+13   0.000   29000.0
 ch2o+ch3=hco+ch4                 5.540e+03   2.810    5860.0
 hco+ch3=ch4+co                   3.000e+11   0.500       0.0
 ch3o(+m)=ch2o+h(+m)              1.995e+13   0.000   27420.0
 c2h4+m=c2h2+h2+m                 9.330e+16   0.000   77200.0
 ho2+o=oh+o2                      1.810e+13   0.000    -397.0
 hco+ho2=ch2o+o2                  1.000e+14   0.000    3000.0
 ch3o+o2=ch2o+ho2                 7.600e+10   0.000    2700.0
 ch3+ho2=ch4+o2                   3.610e+12   0.000       0.0
 hco+o2=co+ho2                    9.096e+12   0.000     410.0
 ho2+h=oh+oh                      1.690e+14   0.000     874.0
 ho2+h=h2+o2                      8.450e+11   0.650    1241.0
 ho2+oh=h2o+o2                    1.450e+16  -1.000       0.0
 h2o2+o2=ho2+ho2                  5.942e+17  -0.660   53150.0
 oh+oh(+m)=h2o2(+m)               1.236e+14  -0.370       0.0
 h2o2+h=h2o+oh                    3.070e+13   0.000    4217.0
 ch4+ho2=ch3+h2o2                 1.120e+13   0.000   24640.0
 ch2o+ho2=hco+h2o2                5.600e+12   0.000   13600.0
 oh+m=o+h+m                       3.909e+22  -2.000  105300.0
 o2+m=o+o+m                       6.473e+20  -1.500  121500.0
 h2+m=h+h+m                       4.570e+19  -1.400  104400.0
 c2h4+m=c2h3+h+m                  6.300e+18   0.000  108700.0
 c2h5+c2h3=c2h4+c2h4              3.000e+12   0.000       0.0
 c2h2+h(+m)=c2h3(+m)              2.345e+15  -0.870    3064.0
 c2h4+h=c2h3+h2                   1.500e+07   2.000    6000.0
 c2h4+oh=c2h3+h2o                 2.020e+13   0.000    5955.0
 c2h4+o=c2h3+oh                   1.510e+07   1.910    3736.0
 c2h2+m=c2h+h+m                   1.000e+14   0.000  114000.0
 c2h2+o2=hco+hco                  4.000e+12   0.000   28000.0
 c2h2+h=c2h+h2                    2.000e+14   0.000   19000.0
 c2h2+oh=c2h+h2o                  6.000e+12   0.000    7000.0
 o+c2h2=c2h+oh                    3.200e+15  -0.600   17000.0
 c2h2+o=ch2+co                    6.700e+13   0.000    4000.0
 c2h+o2=hco+co                    1.000e+13   0.000    7000.0
 c2h+o=co+ch                      5.000e+13   0.000       0.0
 ch2+o2=hco+oh                    1.000e+14   0.000    3700.0
 ch2+o=ch+oh                      1.900e+11   0.680   25000.0
 ch2+h=ch+h2                      2.700e+11   0.670   25700.0
 ch2+oh=ch+h2o                    2.700e+11   0.670   25700.0
 ch+o2=co+oh                      1.350e+11   0.670   25700.0
 ch+o2=hco+o                      1.000e+13   0.000       0.0
 ch3oh+oh=ch2oh+h2o               6.620e+04   2.530    -960.0
 ch3oh+h=ch3+h2o                  6.450e+11   0.000    5310.0
 ch3oh+h=ch2oh+h2                 4.000e+13   0.000    6095.0
 ch3oh+ch3=ch2oh+ch4              4.150e+01   3.170    7170.0
 ch3oh+o=ch2oh+oh                 3.880e+05   2.500    3080.0
 ch2oh+o2=ch2o+ho2                1.000e+14   0.000    5000.0
 ch2oh+m=ch2o+h+m                 1.850e+24  -2.500   34190.0
 c2h3+o2=c2h2+ho2                 1.000e+12   0.000       0.0
 h2o2+o=oh+ho2                    9.550e+06   2.000    3970.0
 c2h2+o=hcco+h                    3.560e+04   2.700    1391.0
 c2h2+oh=ch2co+h                  3.200e+11   0.000     200.0
 ch2co+h=ch3+co                   1.100e+13   0.000    3400.0
 ch2co+o=hco+hco                  1.000e+13   0.000    2400.0
 ch2co+oh=ch2o+hco                2.800e+13   0.000       0.0
 ch2co+m=ch2+co+m                 2.000e+16   0.000   60000.0
 ch2co+o=hcco+oh                  5.000e+13   0.000    8000.0
 ch2co+oh=hcco+h2o                7.500e+12   0.000    3000.0
 ch2co+h=hcco+h2                  7.500e+13   0.000    8000.0
 hcco+oh=hco+hco                  1.000e+13   0.000       0.0
 hcco+h=ch2+co                    1.100e+14   0.000       0.0
 hcco+o=hco+co                    3.400e+13   0.000    2000.0
 c2h6+o2=c2h5+ho2                 4.000e+13   0.000   50900.0
 c2h6+ho2=c2h5+h2o2               1.700e+13   0.000   20460.0
 c2h6+c2h4=c2h5+c2h5              5.000e+11   0.000   60000.0
 ch3+c2h3=ch4+c2h2                7.940e+11   0.000       0.0
 ch3+c2h5=ch4+c2h4                7.940e+11   0.000       0.0
 ch3oh+ch2o=ch3o+ch3o             1.533e+12   0.000   79570.0
 ch2o+ch3o=ch3oh+hco              1.150e+11   0.000    1280.0
 ch4+ch3o=ch3+ch3oh               1.570e+11   0.000    8842.0
 c2h3+h=c2h2+h2                   2.000e+13   0.000    2500.0
……………
```

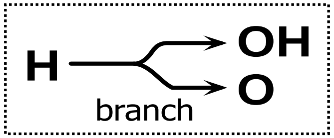
連鎖反応 ー 分岐連鎖反応

H_2-O_2 ー分岐連鎖反応 (連鎖着火)

H + O_2 → **OH** + **O**

O + H_2 → **OH** + **H**

OH + H_2 → H_2O + **H**



net: 2 H_2 + O_2 → **OH** + **H** + H_2O

└ **活性種は消えない (右辺に残る)**

- 連鎖担体 (H, O, OH) 自己増殖
  ➔ 自己加速 ➔ 連鎖着火

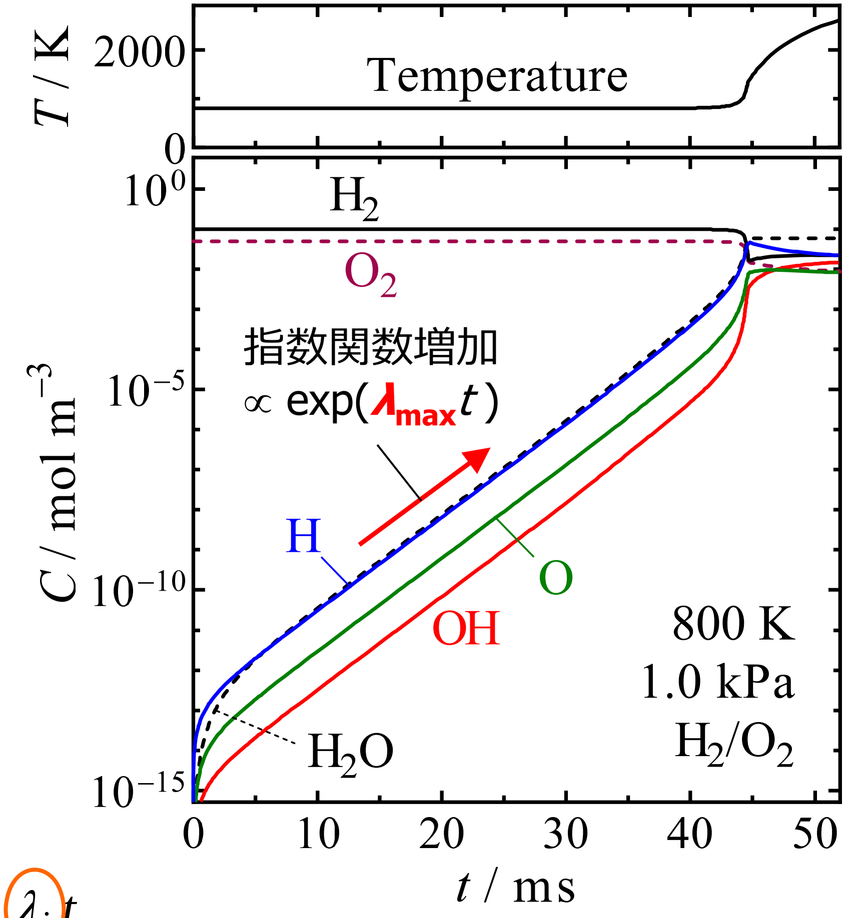
$x = [\mathrm{H}]$, $y = [\mathrm{O}]$, $z = [\mathrm{OH}]$,
$R_1 = k_1[\mathrm{O_2}]$, $R_2 = k_2[\mathrm{H_2}]$, $R_3 = k_3[\mathrm{H_2}]$

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} -R_1 & R_2 & R_3 \\ R_1 & -R_2 & 0 \\ R_1 & R_2 & -R_3 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$$\mathbf{x} = \sum_i a_i \mathbf{s}_i \, e^{\lambda_i t}$$

ヤコビ行列

温度/圧力/組成 が一定 (着火誘導期中) ➔ 不変



$\lambda_{max} > 0$ ... 発散項

自着火限界 ↔ 最大固有値 = 0

$H + O_2 \rightarrow OH + O$

$H + O_2 \rightarrow HO_2$

$O + H_2 \rightarrow OH + H$

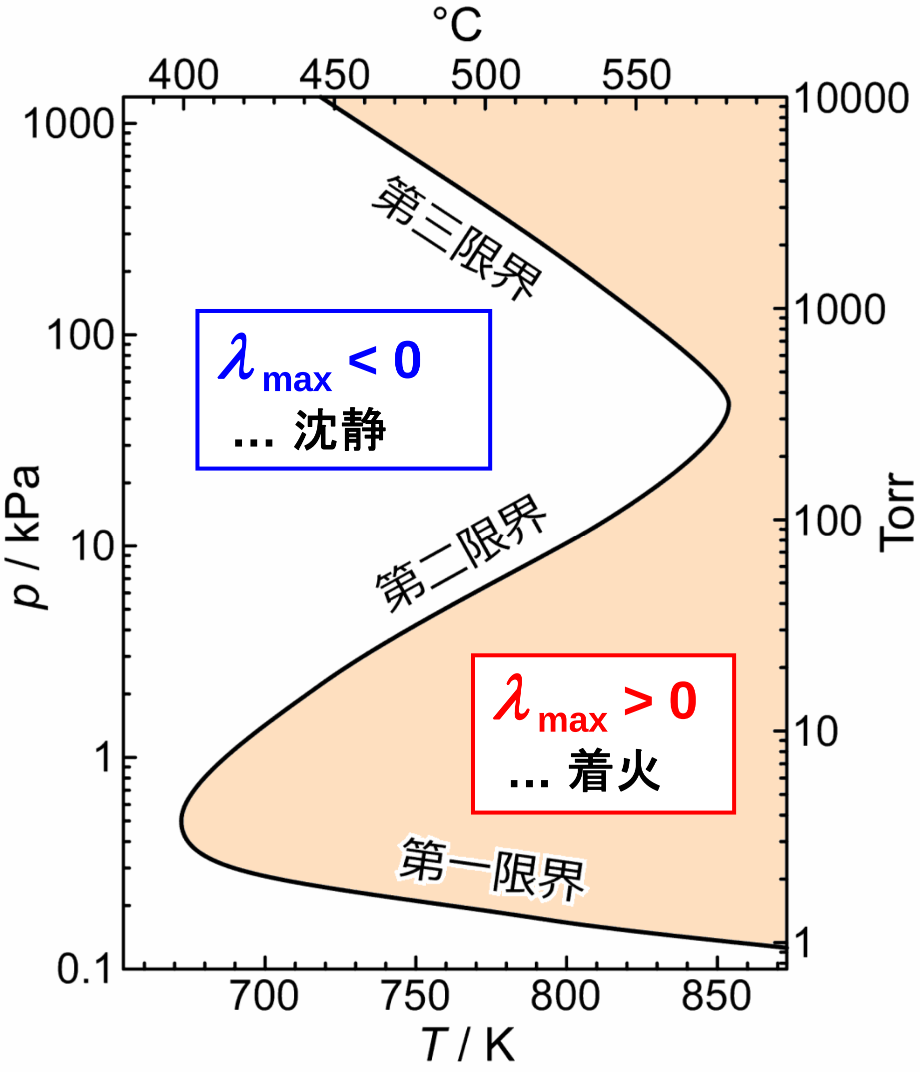
$OH + H_2 \rightarrow H_2O + H$

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} -R_1 - R_4 & R_2 & R_3 \\ R_1 & -R_2 & 0 \\ R_1 & R_2 & -R_3 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

ヤコビ行列

$$\mathbf{x} = \sum_i a_i \mathbf{s}_i \, \mathrm{e}^{\enclose{circle}{\lambda_i} t}$$

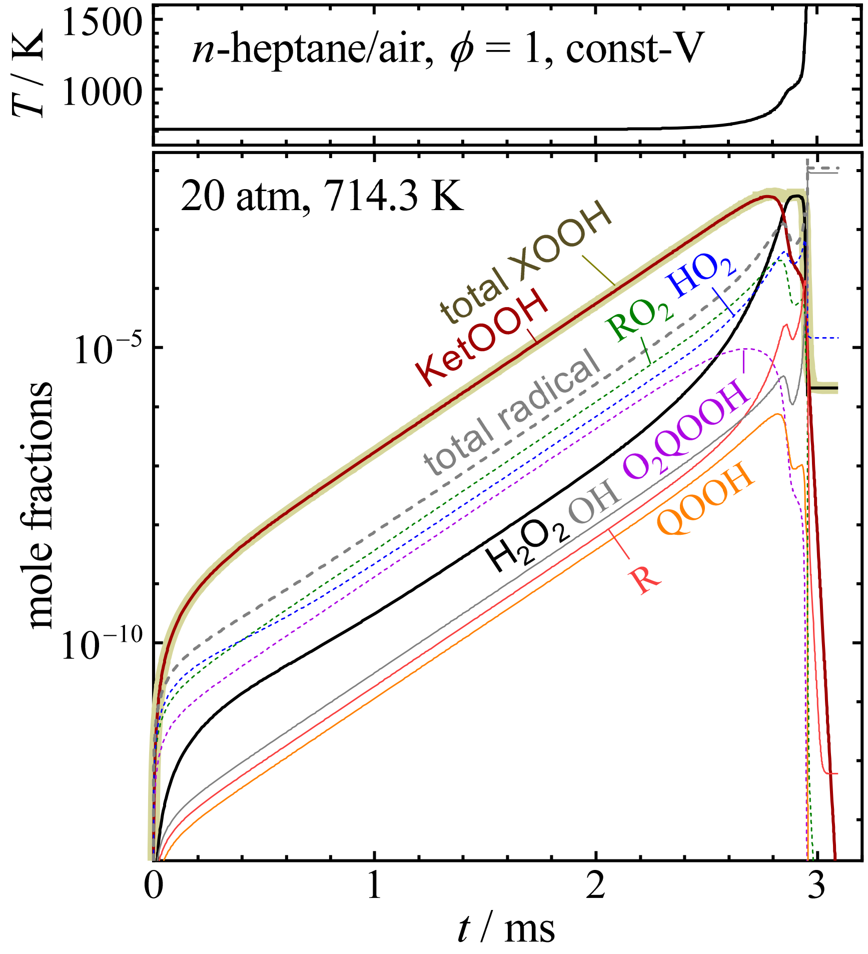
第二限界はこのヤコビ行列で説明可能

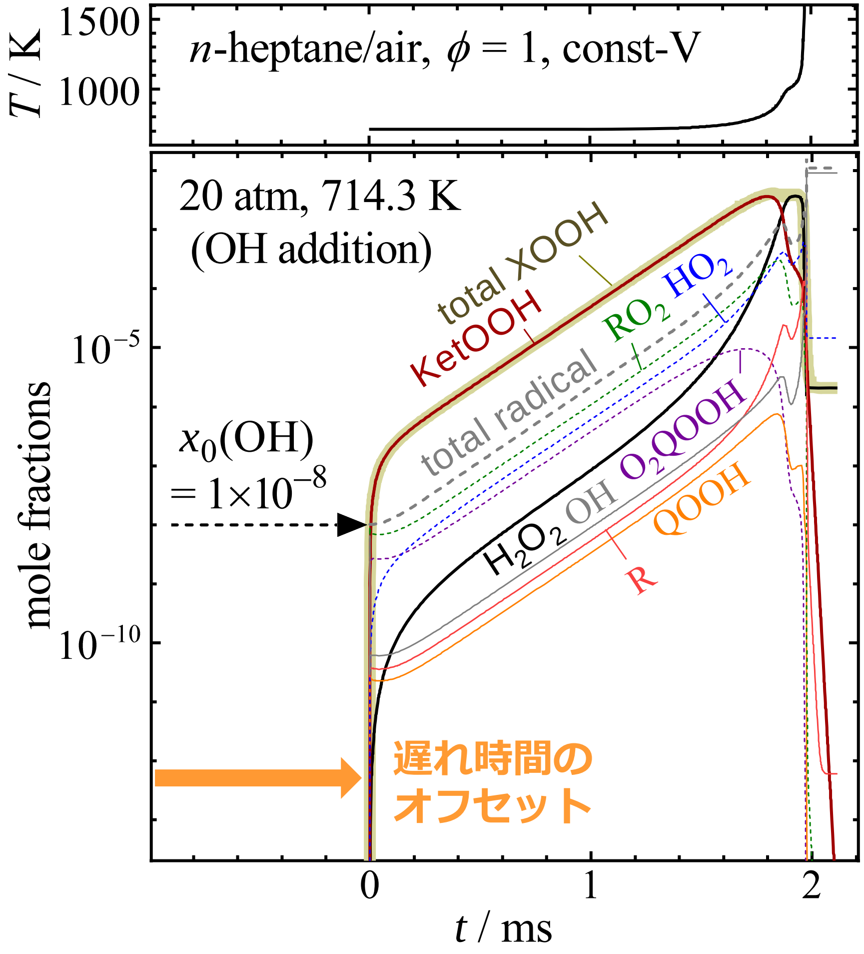


H$_2$:O$_2$ = 2:1 混合気の自着火限界

活性種添加と定常状態

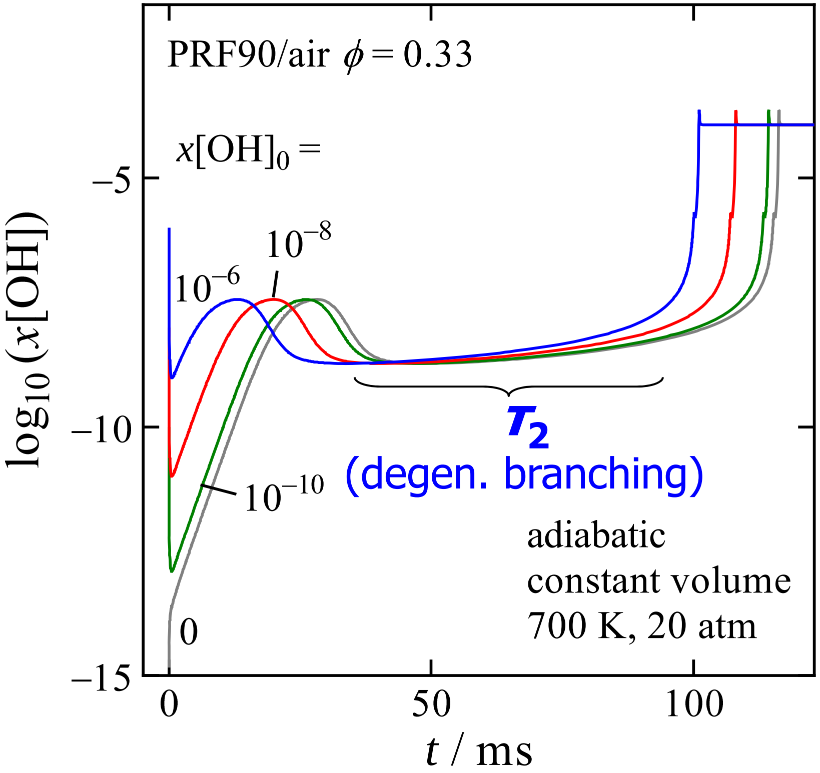
- **活性種添加量 ≈ 全活性種増加量** → 活性種によらない
- OHを添加しても速やかに定常濃度になる → 頑健な定常状態
- 添加効果は時間に指数関数的に減少

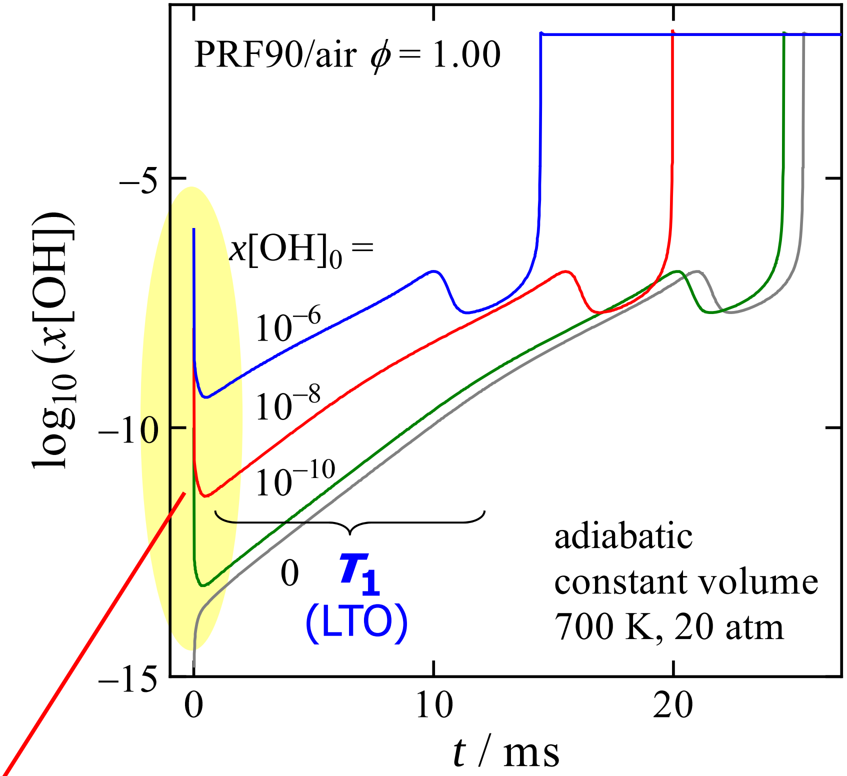




放電の「対数的」効果

- ラジカルの添加は指数関数的増加の始点を変える → **効果は対数的**
- τ_1 (冷炎着火遅れ) のみに影響する
- τ_2 が支配的な場合には**効果が小さい** (例えば低当量比)





$[\mathrm{OH}]_{ss} \approx 10^{-3}\ [\mathrm{OH}]_{added}$

まとめ

– オゾン層破壊

- バックグラウンド(非汚染)大気中の CFC (~1971)
- 連鎖反応の可能性の示唆 (1974)
- 南極環オゾンホール (1985)
- → 規制・代替技術 …「優等生」

– 気候変動

- 温室効果の原理 (19世紀)
- バックグラウンド CO_2 の増加 (1958~)
- 気候変動の証明は困難 … 「劣等生？」

– 燃焼技術

- 燃焼技術 = エネルギー技術
- 数千～ 数万～ の素過程を用いたモデリング = システムの科学
- → 制御の可能性探索