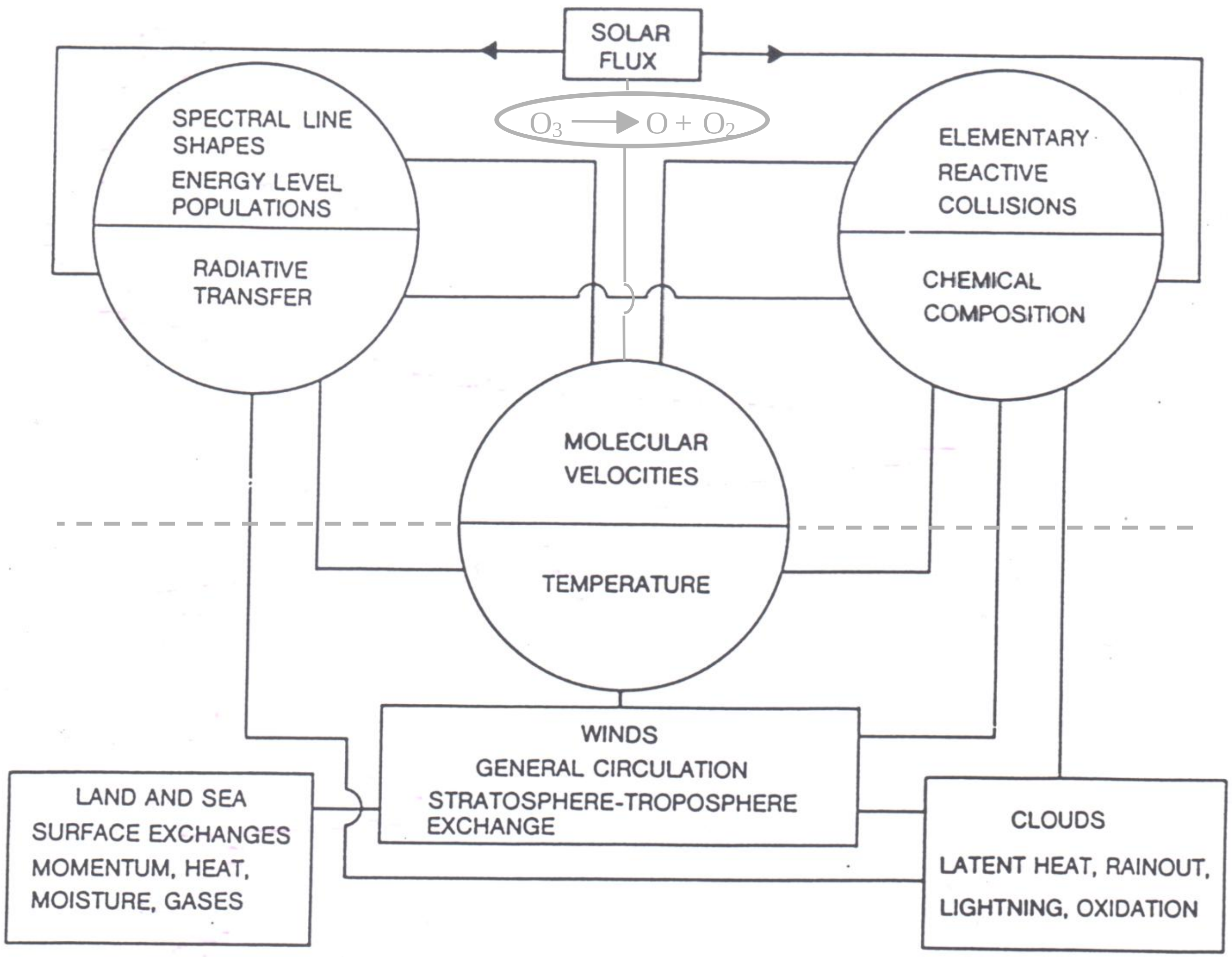
1.2

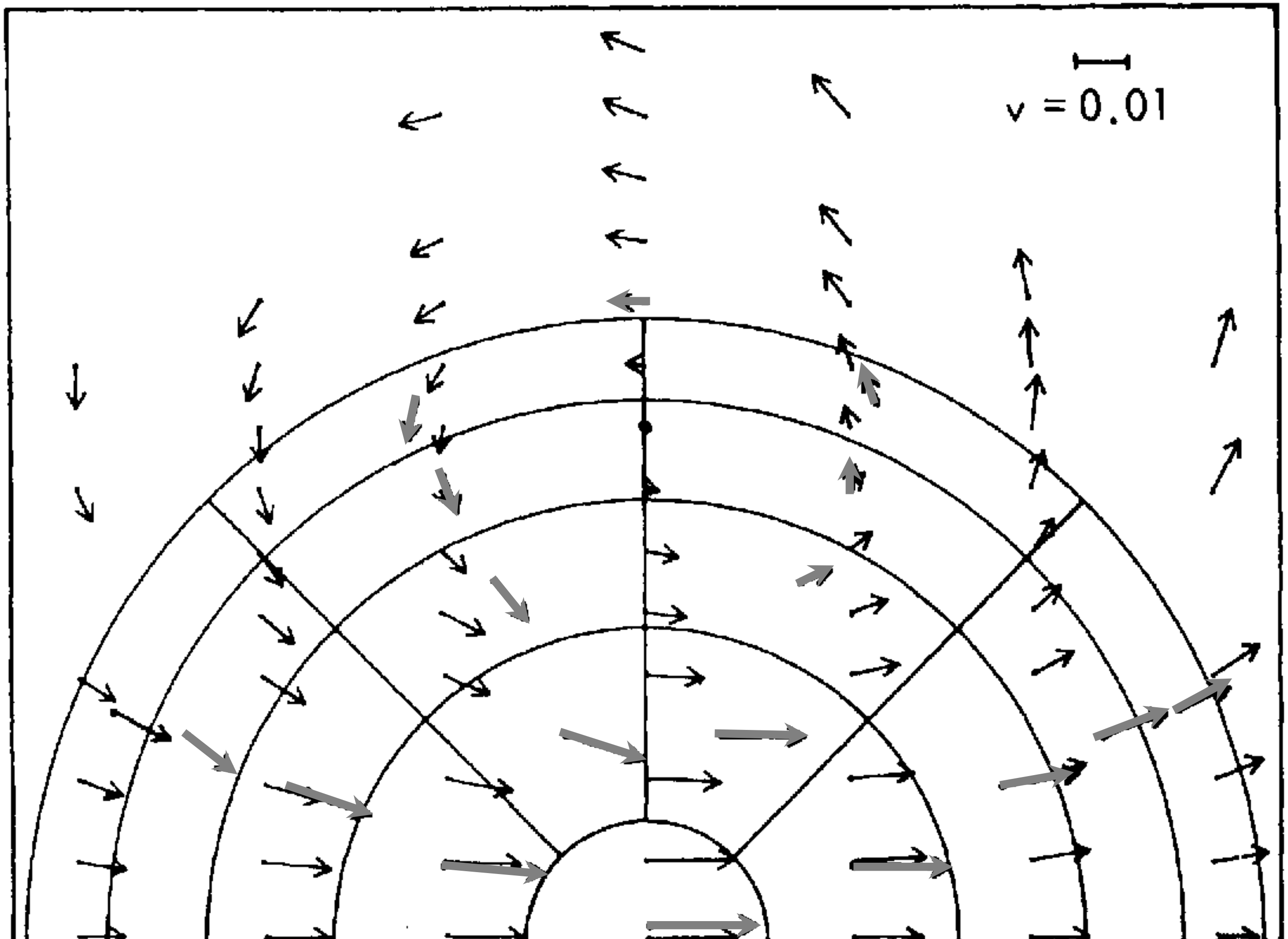
Lecture 1.2 Implications of multifractal scaling for radiative transfer and chemistry

Mutifractal scaling from various research aircraft and some possible consequences for atmospheric composition and chemical kinetics.

The correspondence and coupling of the microscopic and macroscopic processes in the atmosphere.



Alder & Wainwright (1970): A flux applied to an equilibrated population of Maxwellian molecules. Vortices and fluid flow emerge in 10^{-12}s and 10^{-8} m.



CONSEQUENCES:

- **Meteorological models assume that all necessary molecular information is embodied in the gas constant.**

REQUIREMENT:

- **Examine the assumption. After all, if the atmosphere was at equilibrium, we wouldn't be here trying to predict its behaviour.**

CONSEQUENCES:

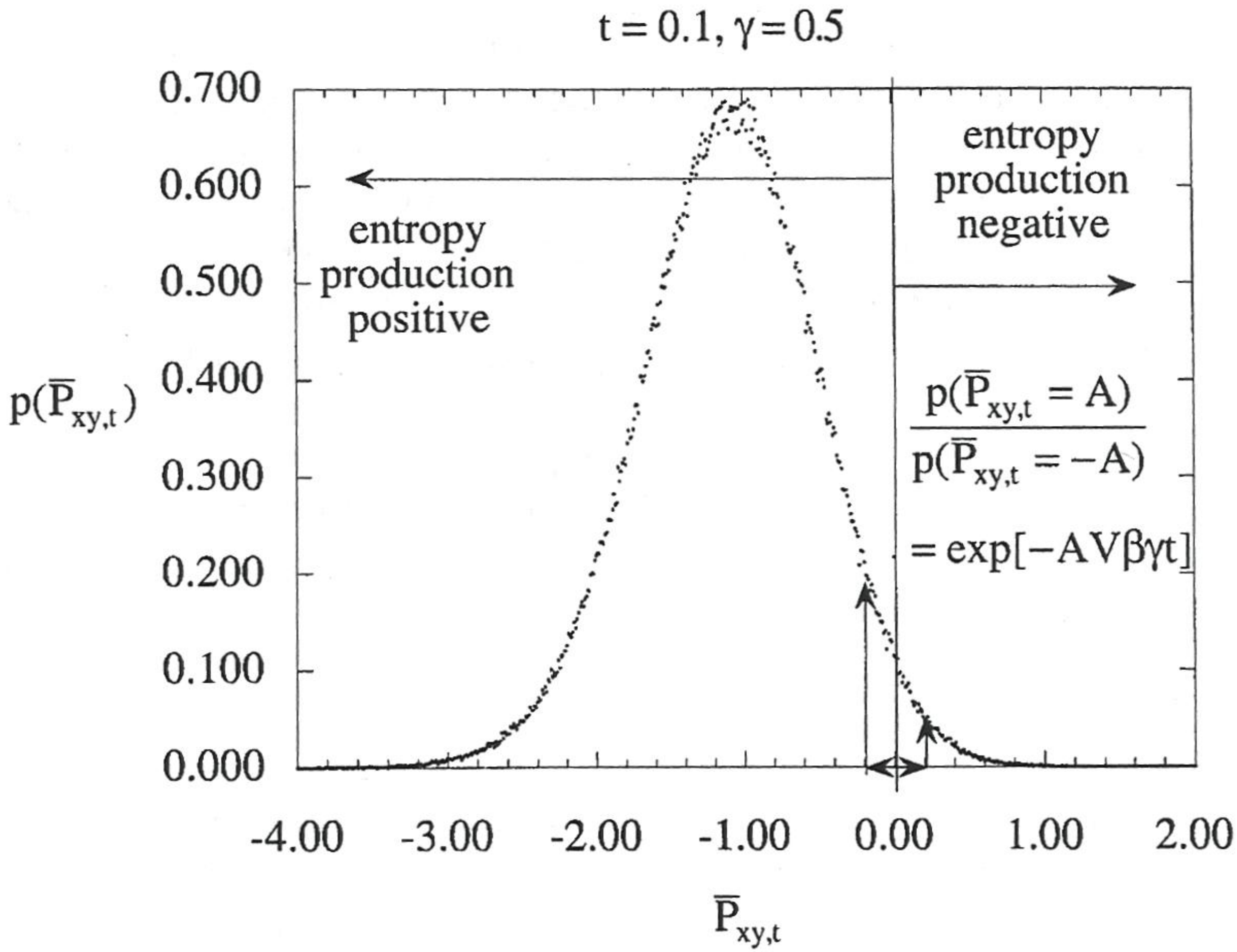
- **No isotropic diffusion at scales > 50 nm**
- **No Maxwell-Boltzmann PDF**
- **No local thermodynamic equilibrium**

REQUIREMENT:

- **Molecular dynamics & Navier-Stokes calculations for an air sample:- do they scale the same?**

Evans & Searles (2002), *Adv. Phys., 51,* 1529-1585. The minority high speed molecules, produce organization ('flow') while the average majority produce dissipation ('temperature').

The Fluctuation Theorem



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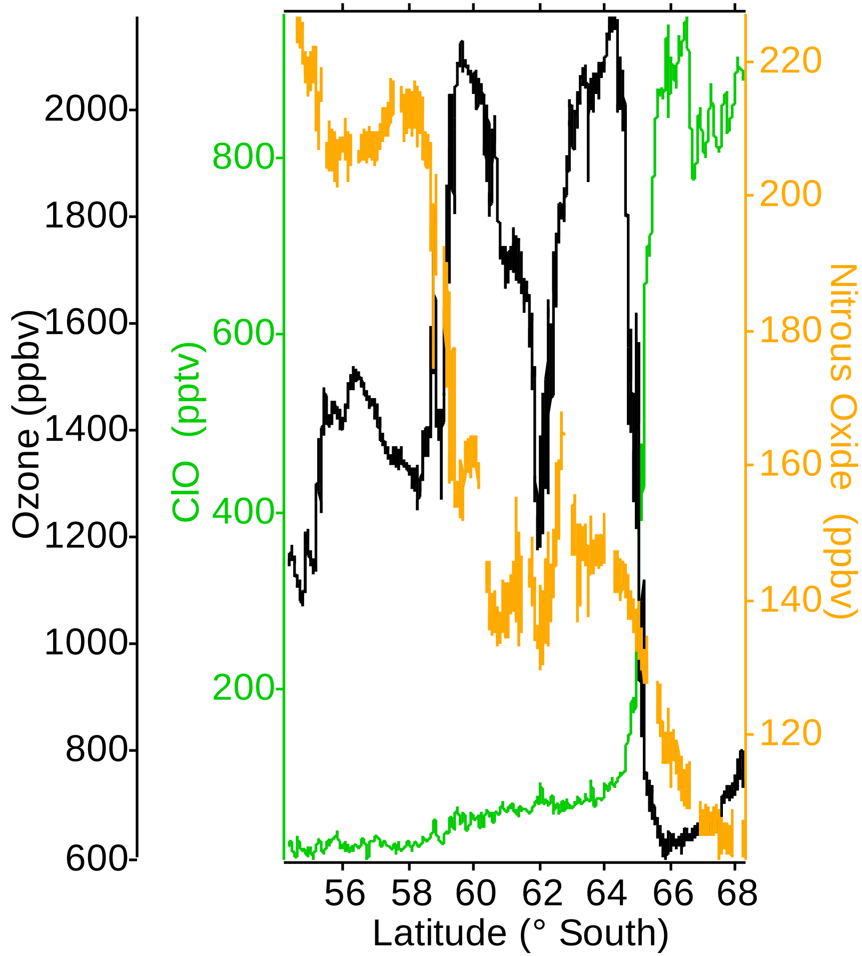
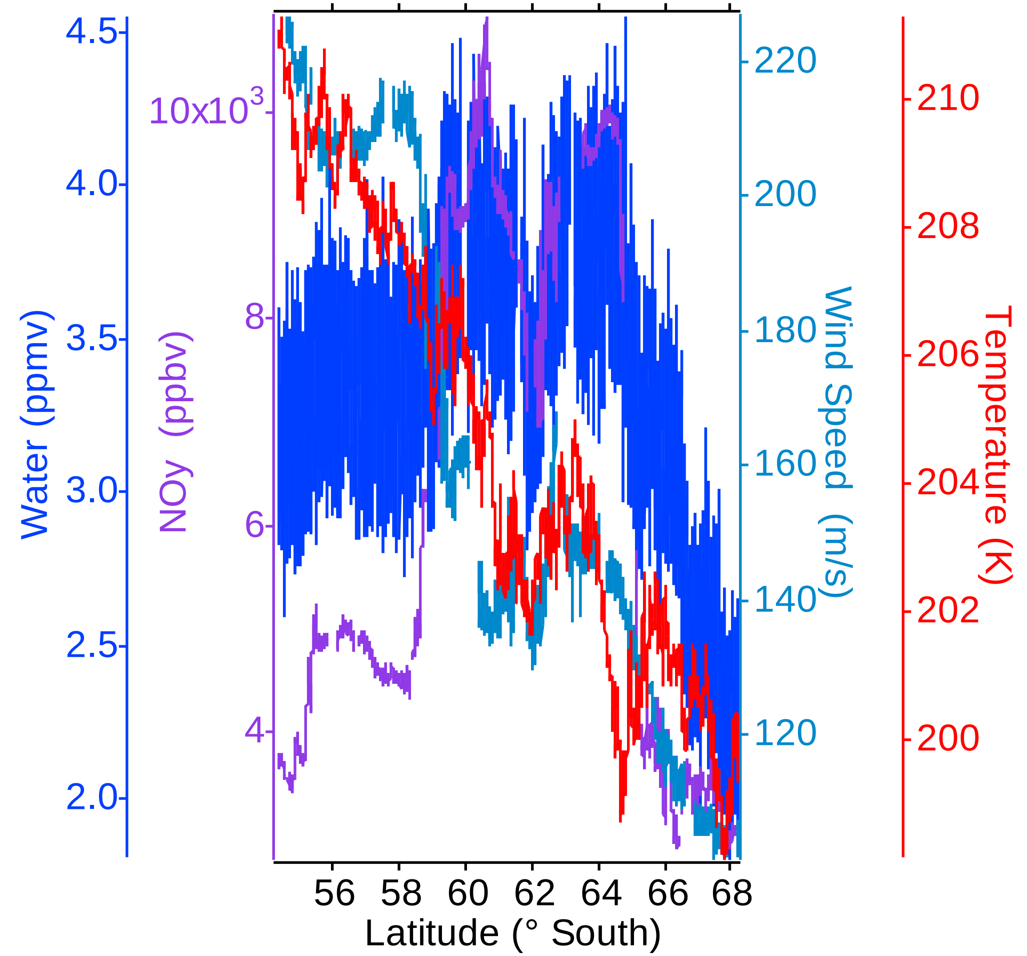
19870922 enddip - begindescent





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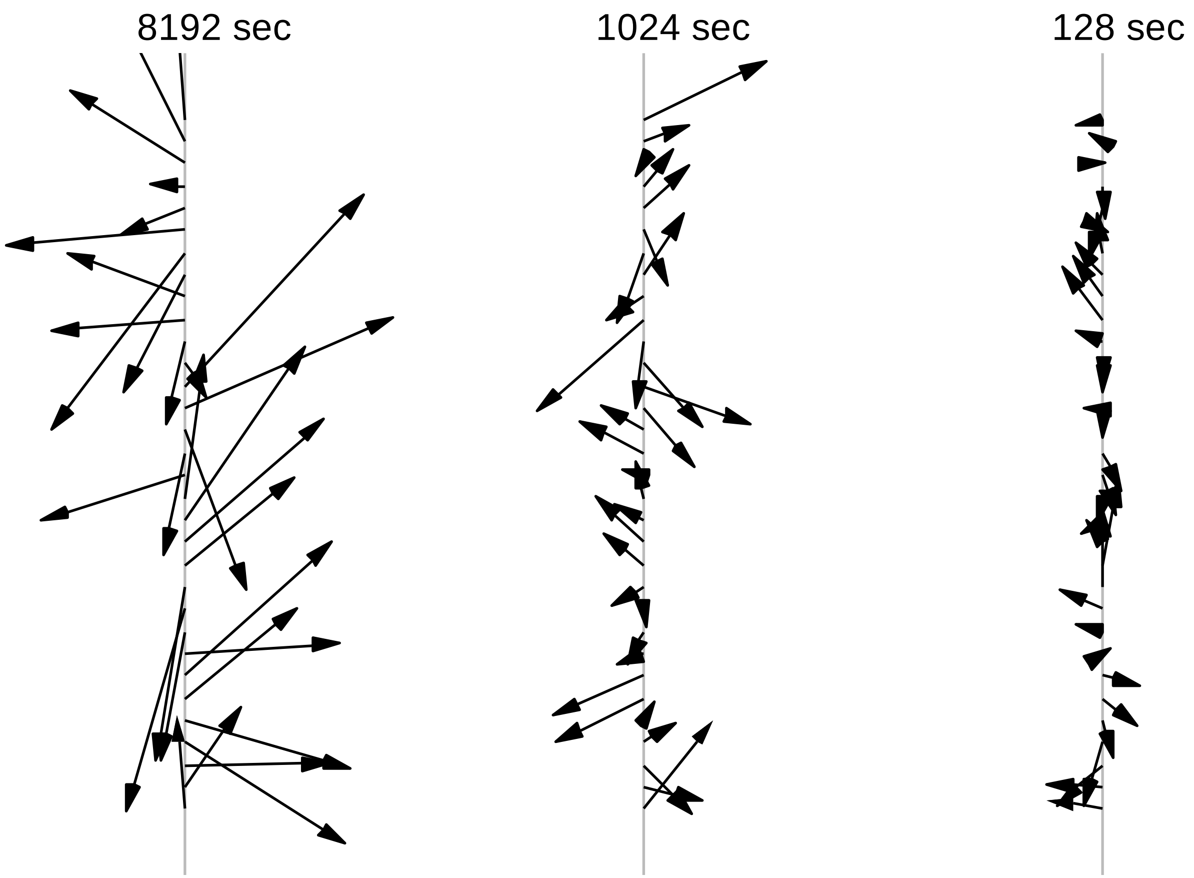
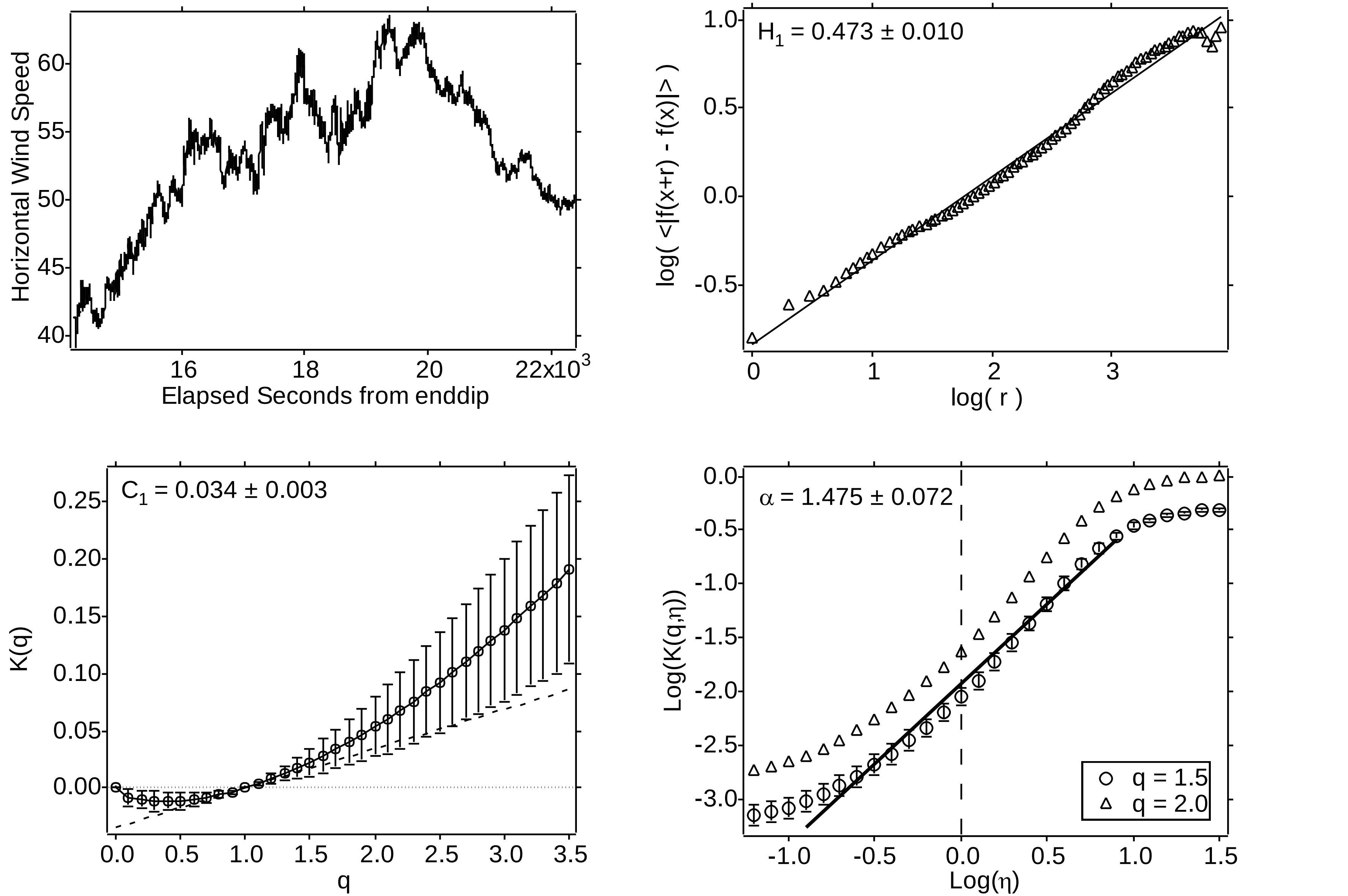
19870922 Wind Vector Differences Centered At 61 S, 68 W



19870922 enddip - begindescent



Slide 27

Generalised Scale Invariance: Exponents

- H Hurst or conservation exponent ($0<H<1$)
- C_1 intermittency exponent ($0<C_1<1$)
- α multifractal exponent ($0<\alpha<2$)

Atmosphere has $H = 0.56$, $C_1 = 0.05$, $\alpha = 1.6$

Gaussian has $H = 0.5$, $C_1 = 0$, $\alpha = 2$

Formal equivalences between scale invariance and statistical thermodynamics:

- **Inverse thermodynamic temperature**

$$q = 1/k_B T$$

- **Partition function**

$$e^{-K(q)} = f$$

- **Gibbs free energy**

$$-K(q)/q = G$$

CONSEQUENCE:

- **Organized flow (winds) is what's left after dissipation has been maximized. It reflects the anisotropies in the boundary conditions.**

- **Scale invariance is equivalent to maximization of entropy production.**

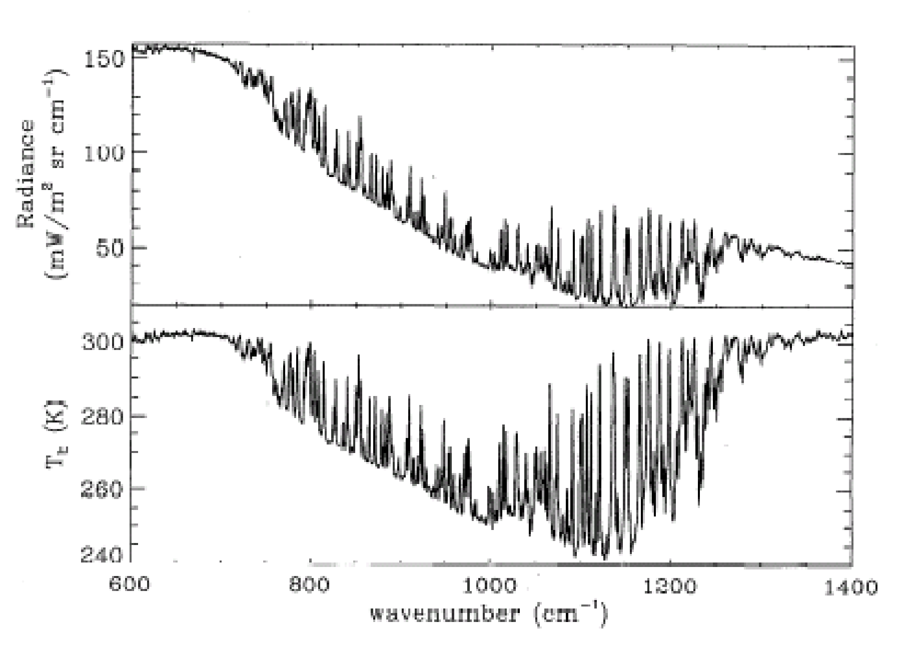
REQUIREMENT:

- **Demonstrate that models minimize Gibbs free energy, *K(q)/q* in generalized scale invariance parlance, and have the right scaling behaviour.**

Colorado
University of Colorado at Boulder

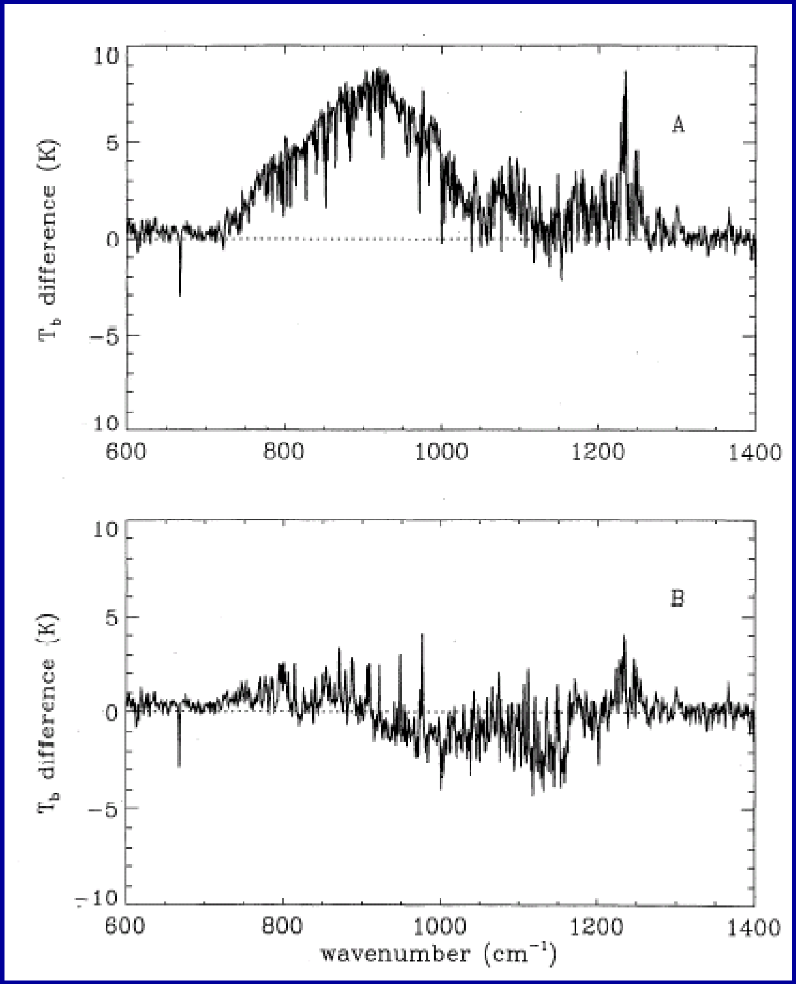
Absorption of IR radiation by water vapour in the atmosphere

CIRES



Highly resolved rovibrational spectrum in the IR and NIR. Continuum absorption known for decades but its description remains controversial.
Cumulative small contributions from spectral lines with “superlorenzian” and ‘sublorentzian”lineshapes. What will non Maxwell-Boltzmann do?
[Courtesy V. Vaida]

Water continuum absorption



The data base on water absorption needed in radiative transfer schemes to quantify the impact of the water continuum on the contemporary Earth radiation budget. Global Climate Models used in weather forecasting and climate predictions use an empirical representation developed over the last 20 years (Clough-Kneizys-Davies + Mlawer-Tobin). Inclusion of CKG in models increases downwelling longwave radiation at the surface by 25% and decreases outgoing longwave radiation by 4%
Research continues in theory, laboratory and field measurements to understand the continuum and its dependence on T and [H_2O]: what will
asymmetric molecular speed distributions do?
[courtesy V. Vaida]

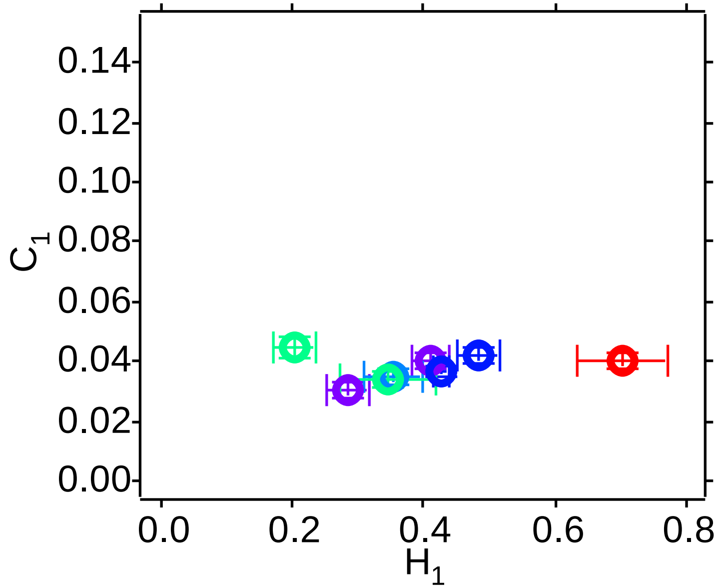
CONSEQUENCE:

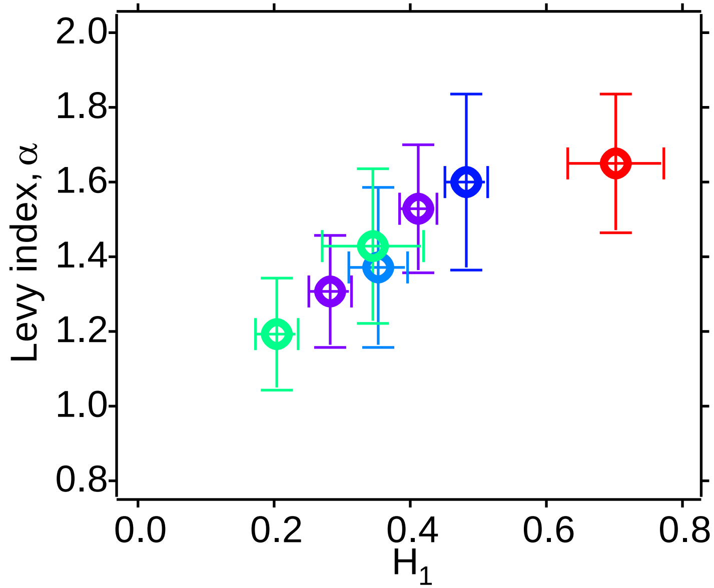
- **Line shapes are influenced by the overpopulation of fast air molecules, especially in the far wings of water vapour lines, where there is a large leverage on greenhouse forcing.**

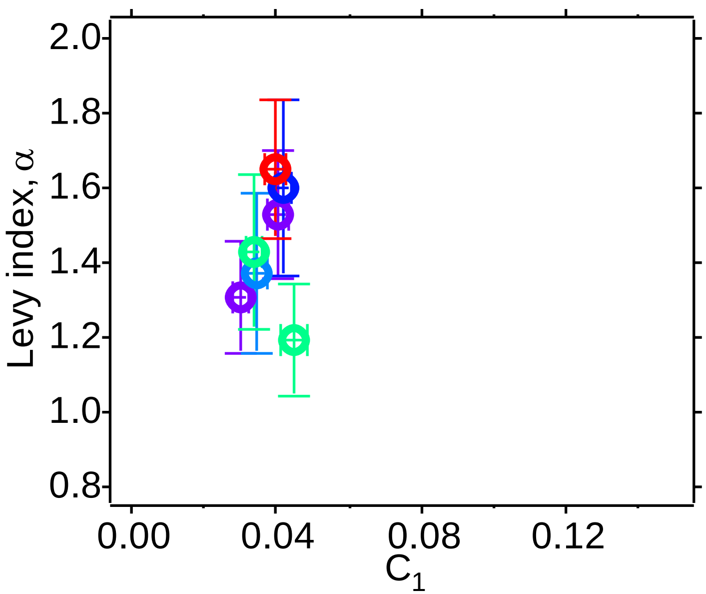
REQUIREMENT:

- **Quantal/MD calculation of line shapes.**
- **Lab & observational investigations.**
- **Use results to recompute atmospheric radiative transfer.**

Universal Multifractal Indices
AAOE Inner Vortex Ozone





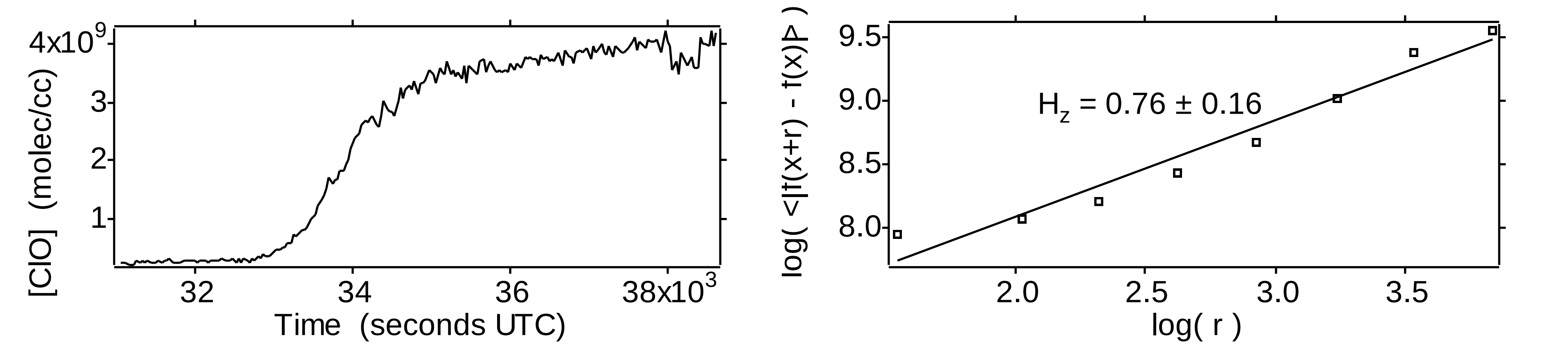


Colored by Year Day

19870830 242
19870902 245
19870904 247
19870909 252
19870922 265

Error bars represent
95% confidence intervals.

20000123



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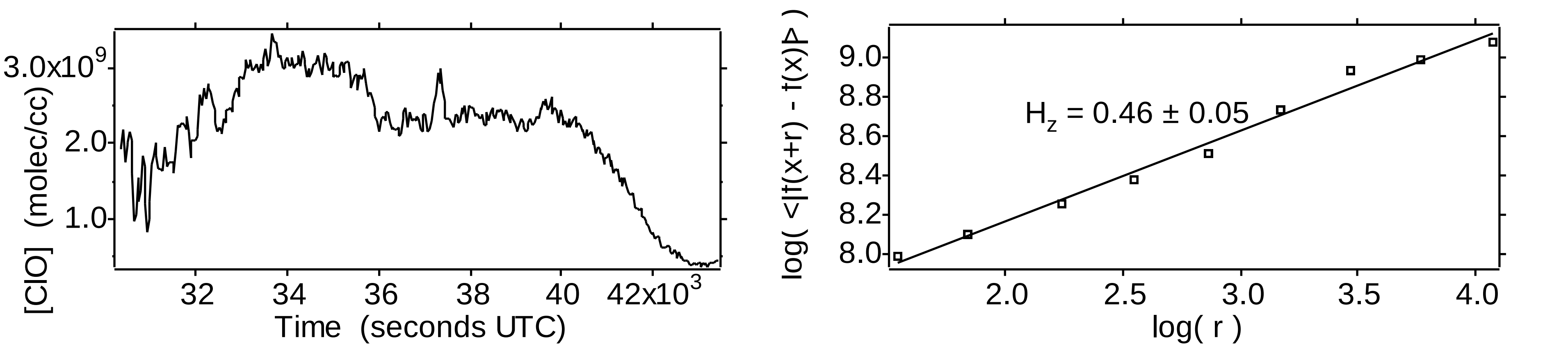

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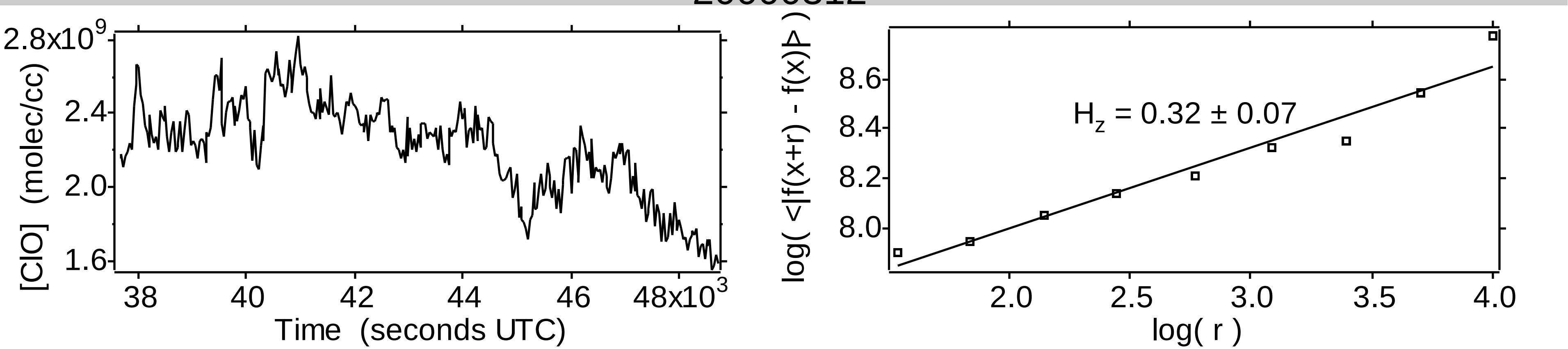


The Law of Mass Action

"In a homogeneous system, the rate of a chemical reaction is proportional to the active masses of the reacting substances."

Guldberg and Waage, 1864, 1867, 1879

$$A+B \longrightarrow C+D$$

The rate of loss of A is given by

$$-d[A]/dt = k[A][B]$$

Here, *k* is the rate coefficient for the reaction.

Evolution of Meaning

$$-d[A]/dt = k[A][B]$$

- Original 19th century formulation: [A] & [B] could have non-integral powers due to complex nature of reaction, consisting of sequence of unknown elementary collisional steps.
- Modern usage: A & B are collision partners. *k* is microscopic, referring to a Maxwell-Boltzmann gas. Both reactants have random access to the entire reaction volume in 3 dimensions. *k* is mostly measured with lab apparatus designed to eliminate fluid mechanical fluctuations in a volume with true diffusion as the only transport process.

A Simple Ozone Loss Mechanism

PSC → $\{Cl_2 + h\upsilon$	$\rightarrow$	$Cl + Cl\}$	R1
$2(Cl + O_3$	$\rightarrow$	$ClO + O_2)$	R2
$ClO + ClO + M$	$\rightarrow$	$Cl_2O_2 + M$	R3
$Cl_2O_2 + h\upsilon$	$\rightarrow$	$Cl + ClO_2$	R4
$ClO_2 + M$	$\rightarrow$	$Cl + O_2 + M$	R5

Nett: $2O_3 \longrightarrow 3O_2$

Rate determining step is usually R4. At steady state:

$$k_3[ClO]^2[M] = J_4[Cl_2O_2]$$

What Volume?

$$k_3[ClO]^2[M] = J_4[Cl_2O_2]$$

- To what volume does this rate equation apply?
- Scale invariance means there are fluctuations in concentration on all scales - how often do they encounter each other? Not at the same rate as if ‘true’ 3-D diffusion was operative.
- Alder’s results show that molecular diffusion guarantees nothing. 10^{-8} metres is 15 orders of magnitude less than the scale of the vortex.

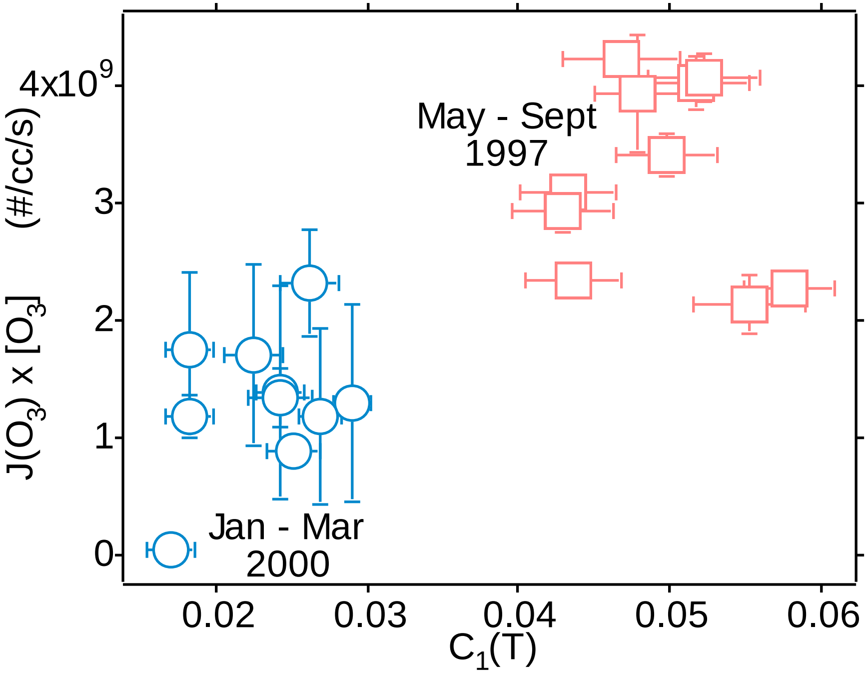
CONSEQUENCES:

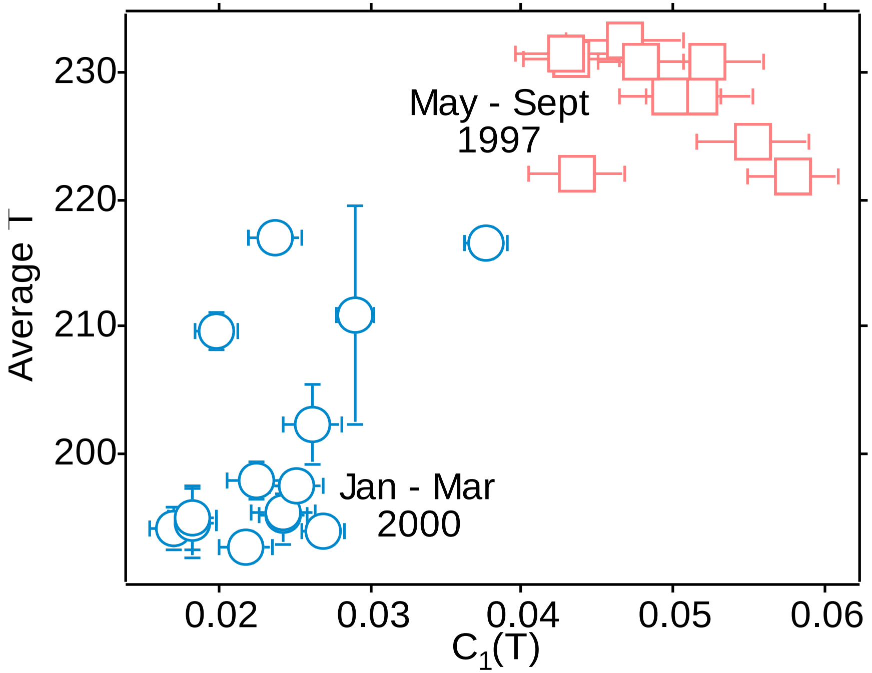
- **Coupling of chemistry, radiation and dynamics happens at very small scales.**
- **Averaging over large volumes to get reaction rates, e.g. the vortex or a cloud, is not justified. *H*(ClO) changed with time January to March.**

REQUIREMENT:

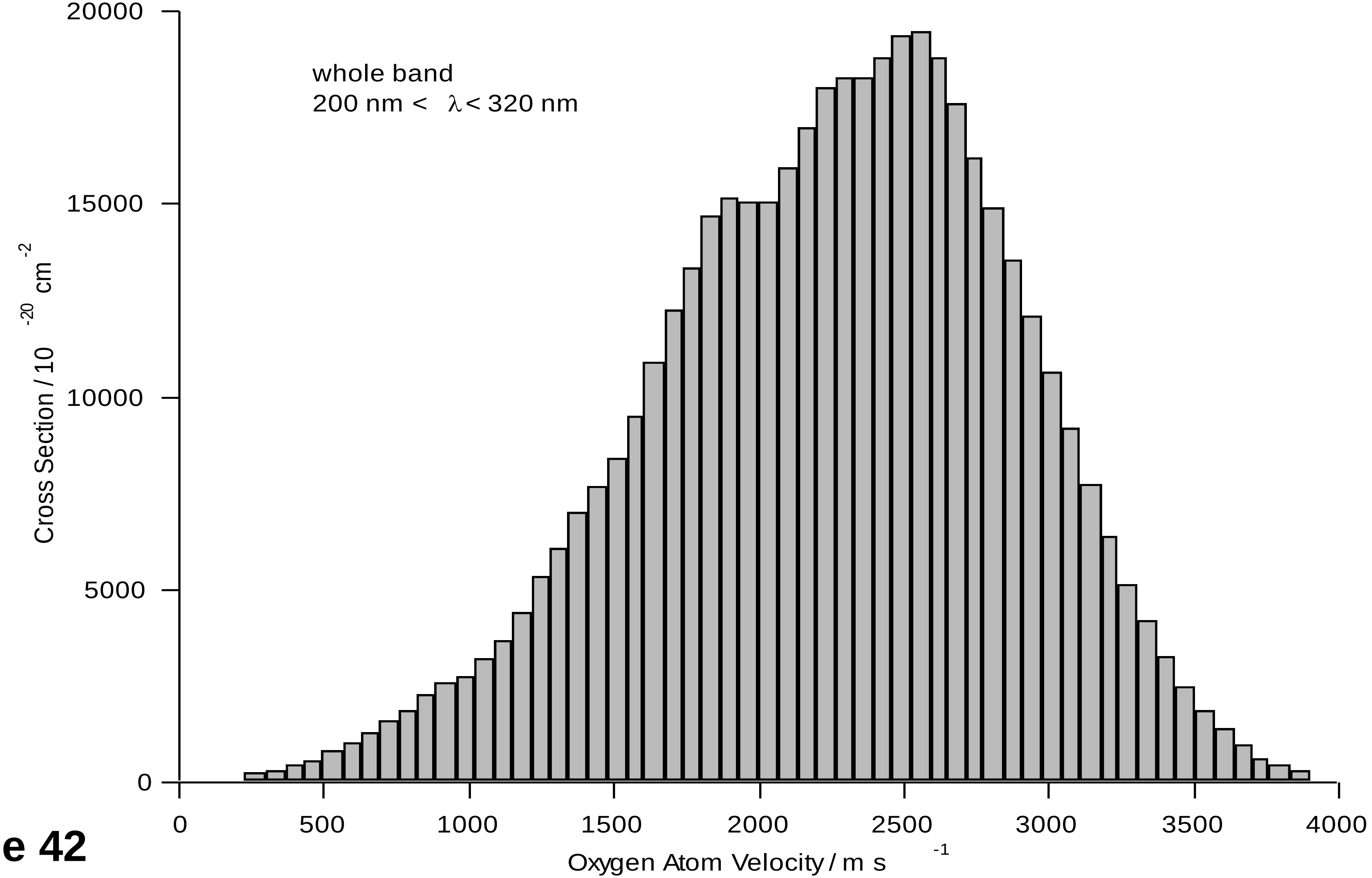
- **Molecular dynamics modelling of the chemistry of an air sample with and without reaction, to examine effects on scaling behaviour.**

Intermittency of temperature as function of $J(O_3)$ & T
Arctic summer and winter

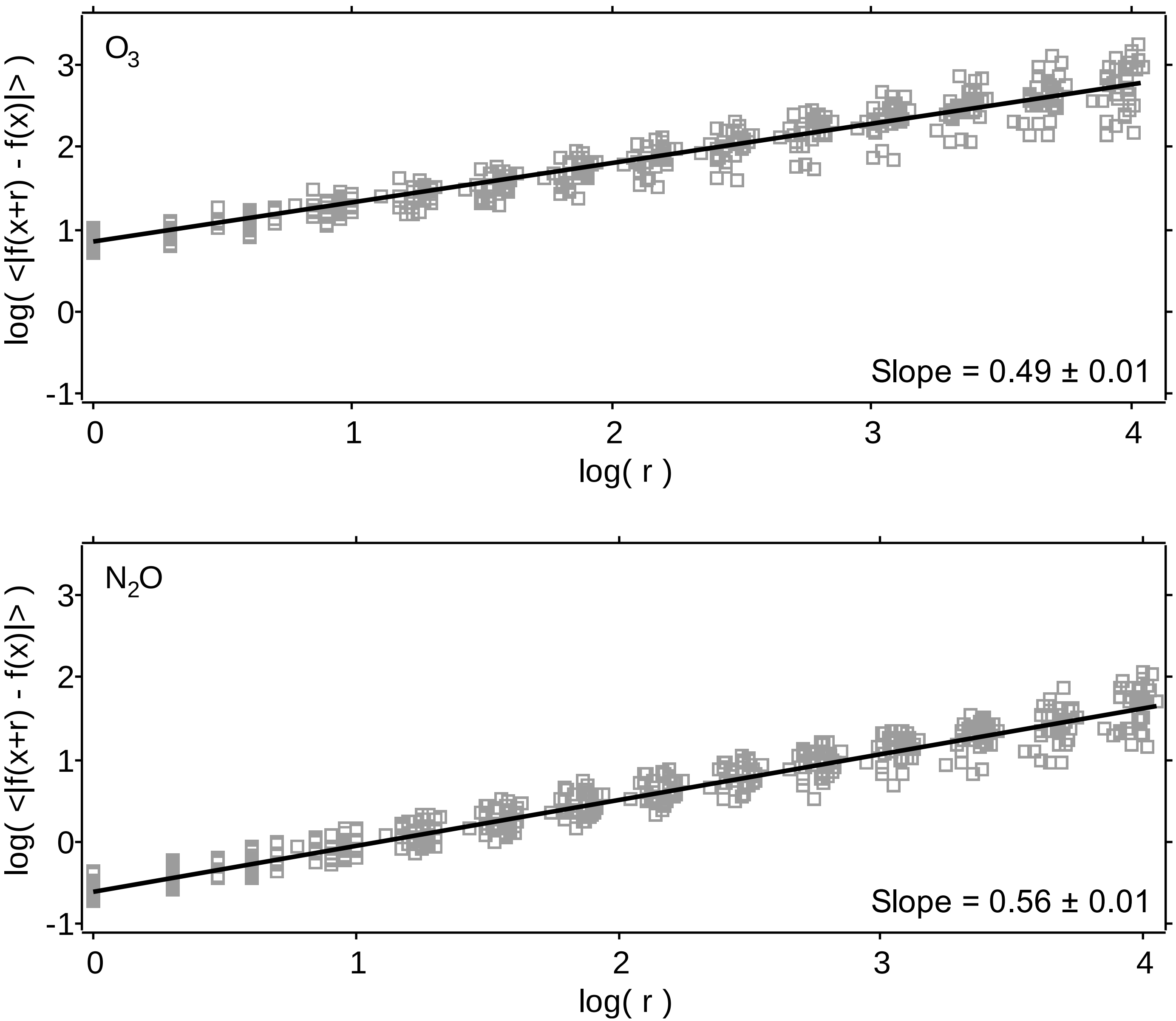




Baloïtcha & Balint-Kurti (2005), *PCCP, 7,* 3829-3833. Speed distribution of photofragments, O_3 photodissociation, Hartley band.



All ER-2 ozone & nitrous oxide, 59˚N-70˚S, heavy SH weighting



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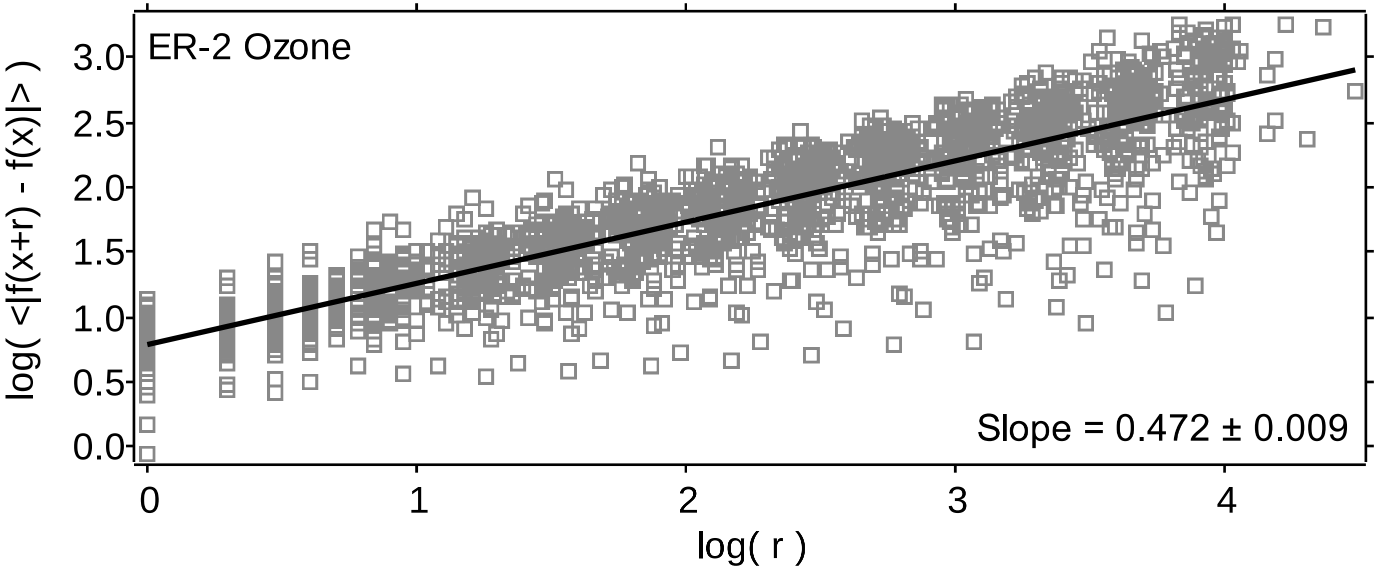
All ER-2 'horizontal' segments >2000 s, 1987-2000



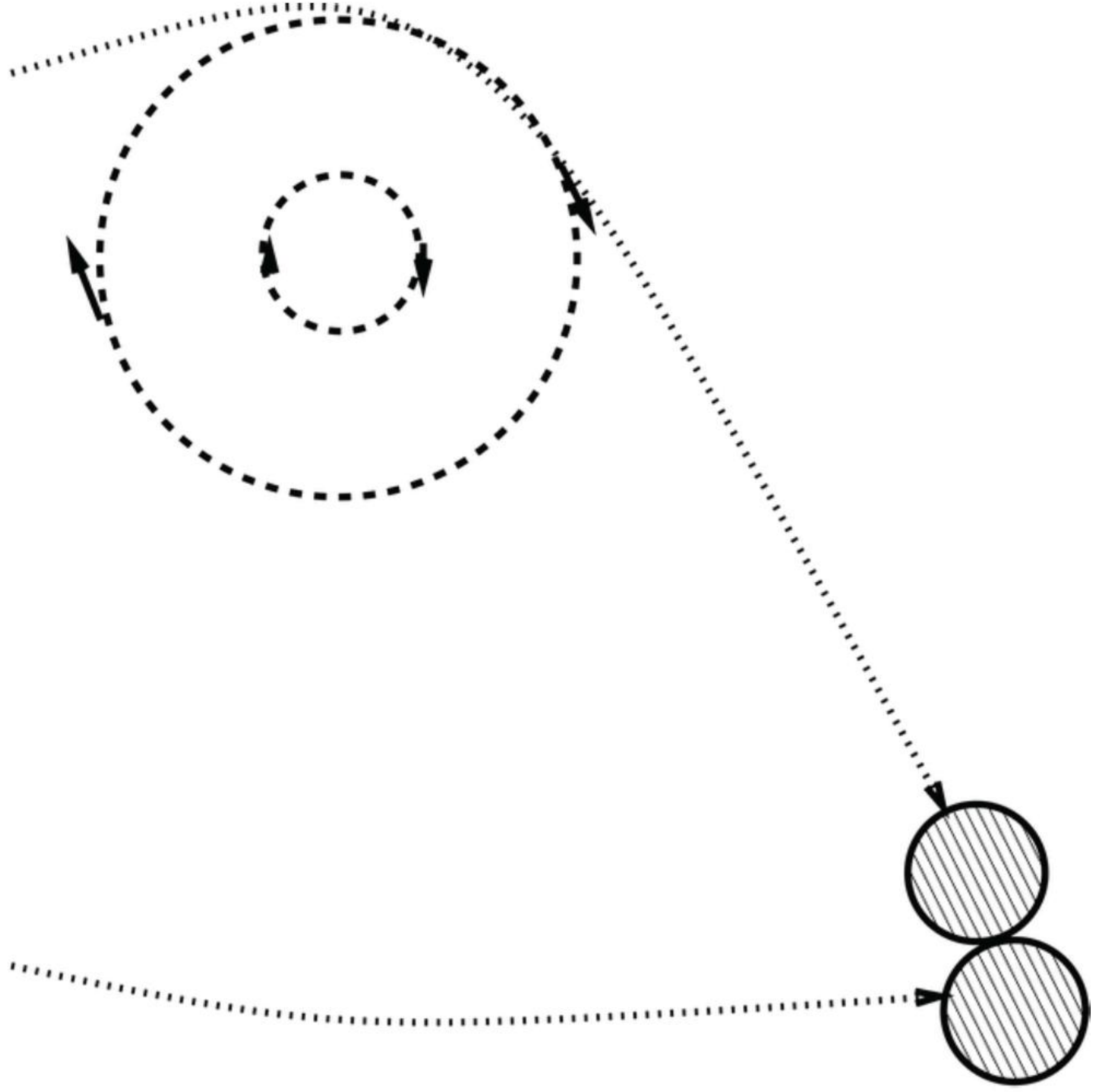
- All points with *H* < 0.56 correspond to ozone loss régimes.
- Lowest values are inside vortex.
- Highest values are in Antarctic recovery, late September.
- Consistent with ClO behaviour in Arctic 2000, slide 34.
- ***H* = 0.56 is tracer (passive scalar) behaviour.**
- ***H* > 0.56 is source behaviour.**
- ***H* < 0.56 is sink behaviour.**

CONSEQUENCES:

- **Fast recoiling photofragments are not instantly thermalized; they convert solar photon energy into vorticity.**
- **Sink species have low *H* exponents, corresponding to minimization of Gibbs free energy via dissipation. Source species have high *H*, corresponding to production of organization. Tracers have *H* = 5/9.**

REQUIREMENT:

- **Calculate speed distribution of ground state O(^{3}P) atoms from Huggins and Chappuis bands.**
- **Models have to pass these tests.**



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CONSEQUENCE:

- **Aerosol and cloud physics affected by non-LTE, molecular speed distributions and turbulent scaling structure.**

REQUIREMENT:

- **Systematic, *a priori* molecular dynamics calculations to examine magnitudes and sensitivities.**

SUMMARY: Lecture 1 of 5

•Alder-Wainwright mechanism converts solar photon energy directly into vorticity.

•Fluid flow emerges in picoseconds and on 10 nm space scale.

•No Maxwell-Boltzmann PDFs, no LTE.

•Non-equilibrium statistical mechanics applies.

•Manifold consequences for chemistry, radiation, cloud physics and dynamics have the potential to put theoretical & physical chemistry, and statistical physics, at the heart of climate and global change.