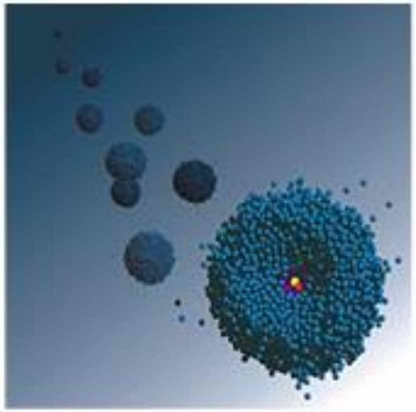
Brioni 2008, 29. August 2008

Are Hydrogen Clusters Superfluid?



J.Peter Toennies

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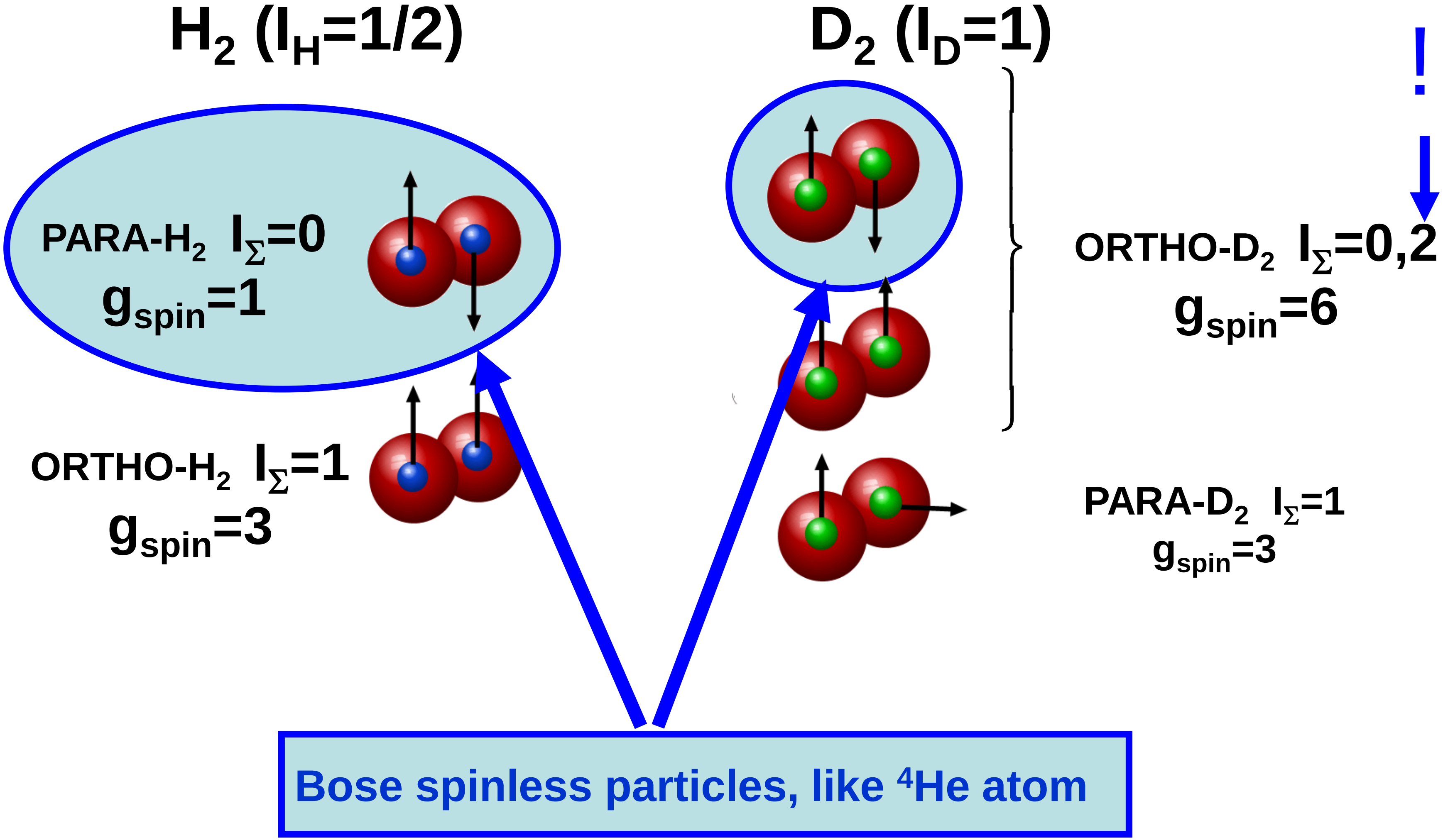
Max Planck Institut für Dynamik und Selbstorganisation

Göttingen, Germany

Hydrogen Isotopomers



H_2 ($I_H=1/2$)

PARA-H_2 $I_\Sigma=0$
$g_{spin}=1$

ORTHO-H_2 $I_\Sigma=1$
$g_{spin}=3$

D_2 ($I_D=1$)

!

ORTHO-D_2 $I_\Sigma=0,2$
$g_{spin}=6$

PARA-D_2 $I_\Sigma=1$
$g_{spin}=3$

Bose spinless particles, like ^{4}He atom

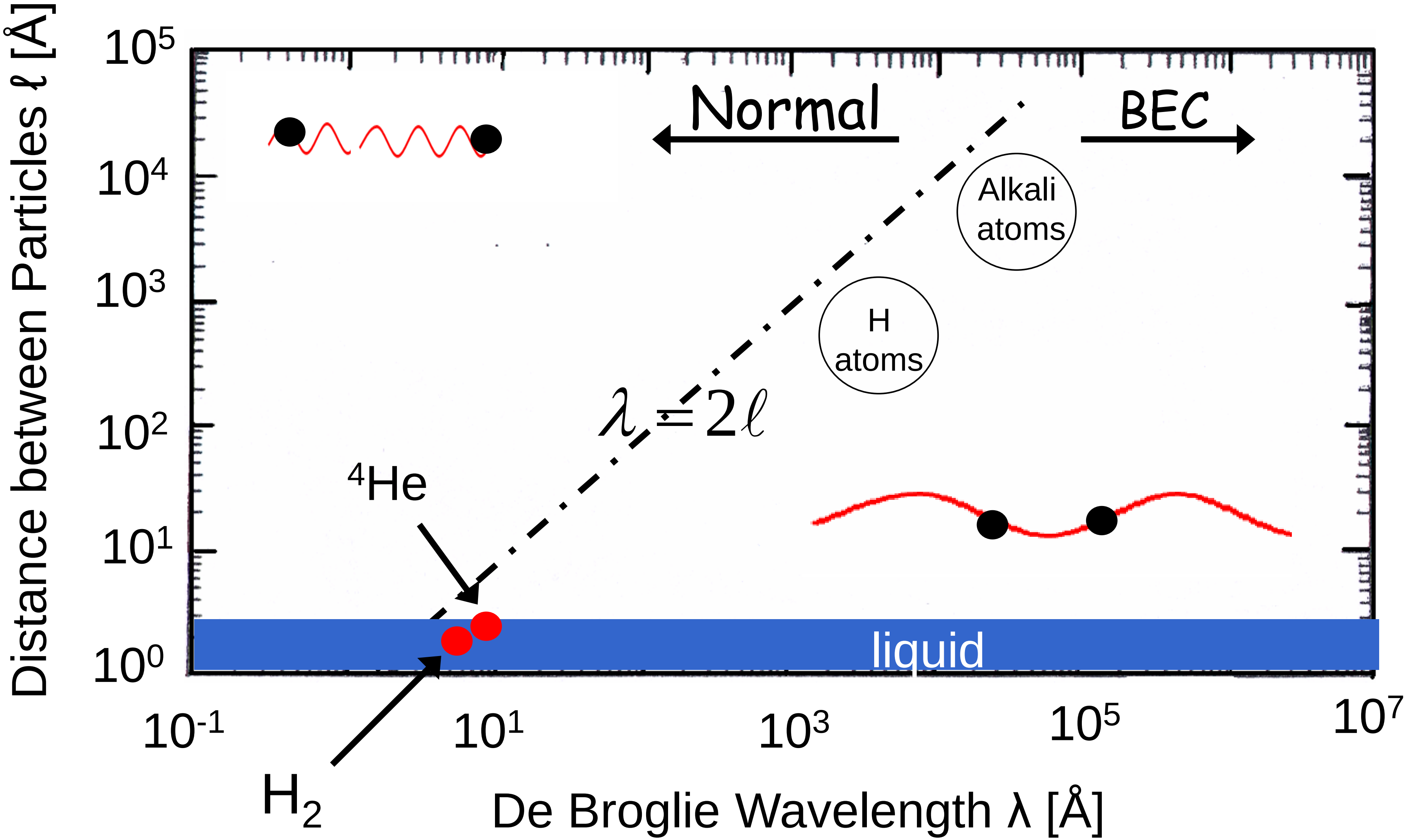
Bosons

Bosons Have Unique Coherent Macroscopic Quantum States

Particle	**Coherence seen in**	
cooper pairs	superconductivity	
alkali gases hydrogen atom gases metastable He gases	BEC	
^{4}He liquid	superfluidity	
^{4}He solid	supersolid	?
^{3}He pairs (liquid)	superfluidity	
supercooled H_2	superfluidity	?
nucleon pairing	nuclei	
Higgs Boson	elementary particles	
Stars	Pulsar glitches	

BEC vs SF

Bose-Einstein Condensation vs. Superfluidity



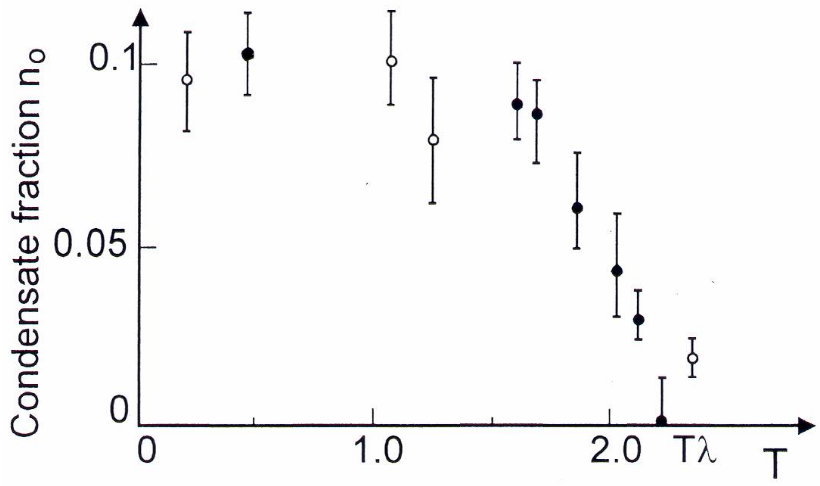
Dalfovo

BEC and Superfluidity:

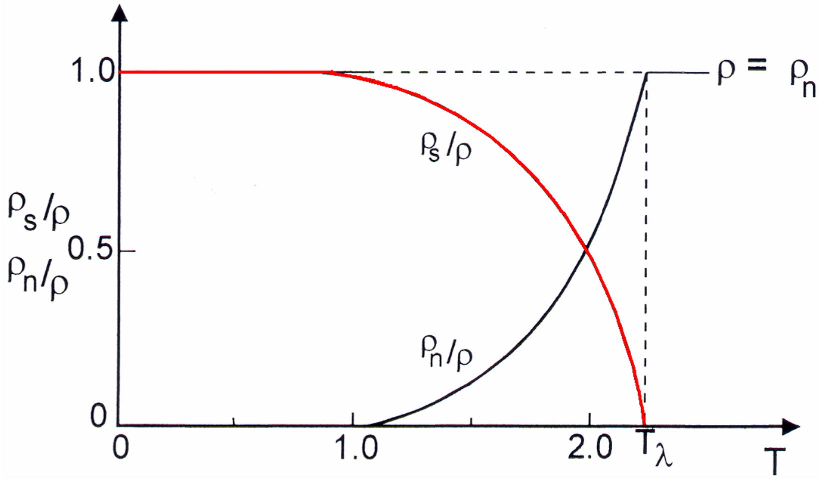
………, the explicit connection between superfludity and BEC is not trivial and has been the object of a longstanding and deep investigation in the last decades, mainly for its importance in understanding the physics of liquid helium

Dalfovo, Giorgini, Pitaevskii and Stringari: Rev. Mod. Phys. **71** (1991)

In He^4 Condensate Fraction is only 10%



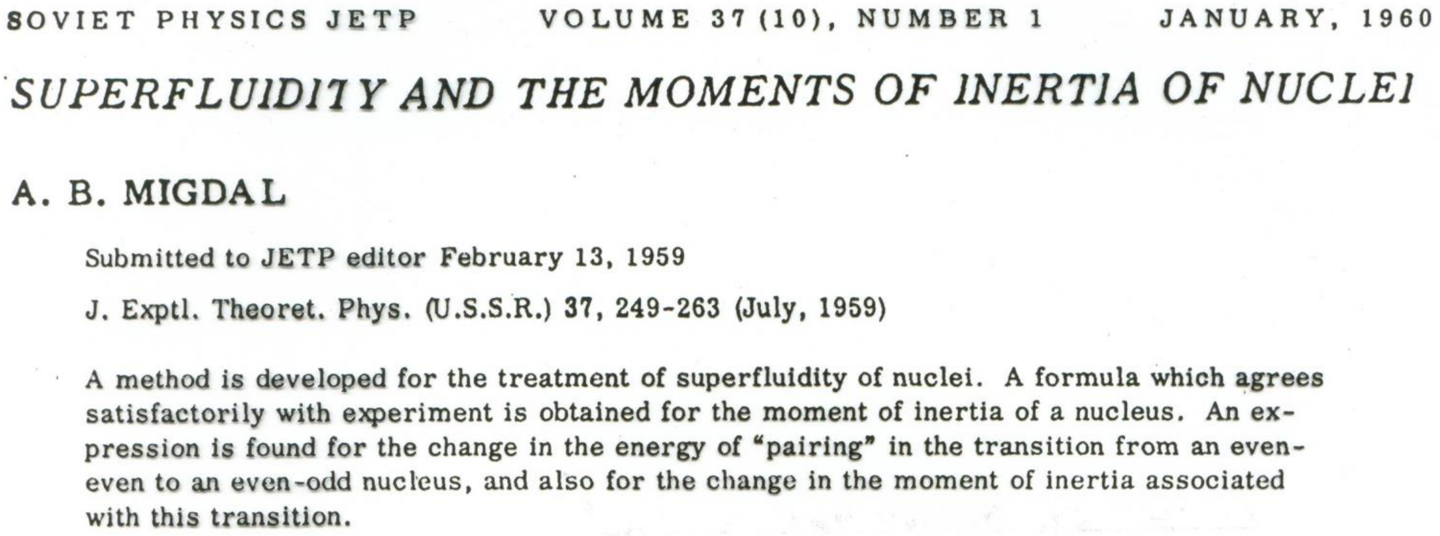
Superfluid Fraction approaches 100%



Superfluidity is usually regarded as a **macroscopic** phenomenon!!

Ginzburg

There are Well Known **Microscopic** Manifestations of Superfluidity



SOVIET PHYSICS JETP VOLUME 37 (10), NUMBER 1 JANUARY, 1960

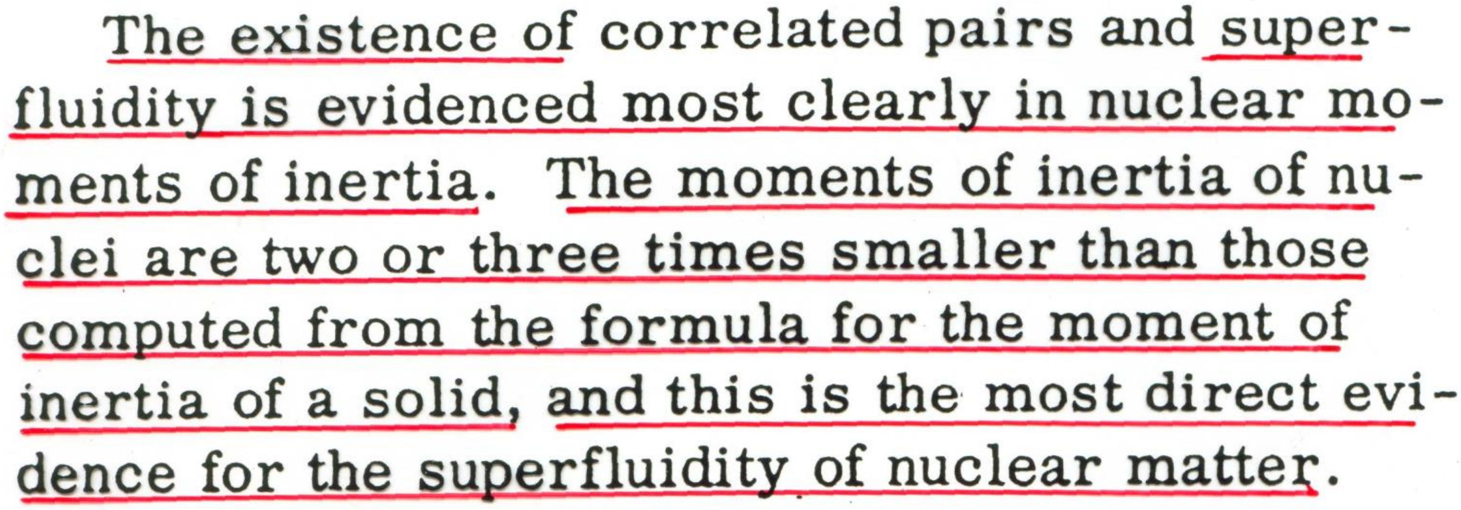
SUPERFLUIDITY AND THE MOMENTS OF INERTIA OF NUCLEI

A. B. MIGDAL

Submitted to JETP editor February 13, 1959

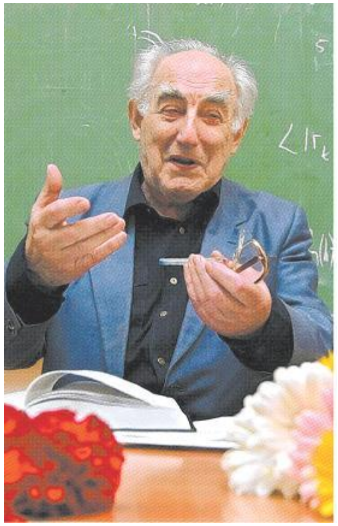
J. Exptl. Theoret. Phys. (U.S.S.R.) 37, 249-263 (July, 1959)

A method is developed for the treatment of superfluidity of nuclei. A formula which agrees satisfactorily with experiment is obtained for the moment of inertia of a nucleus. An expression is found for the change in the energy of "pairing" in the transition from an even-even to an even-odd nucleus, and also for the change in the moment of inertia associated with this transition.



The existence of correlated pairs and superfluidity is evidenced most clearly in nuclear moments of inertia. The moments of inertia of nuclei are two or three times smaller than those computed from the formula for the moment of inertia of a solid, and this is the most direct evidence for the superfluidity of nuclear matter.

Search for Superfluidity in para-H_2



In 1972 Vitali Ginzburg (Nobel Prize 2003) and Alexander Sobyanin predicted that liquid hydrogen can become superfluid.

Ginzburg and Sobyanin, JETP Lett. 15, 242 (1972)

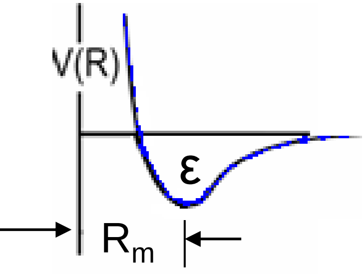
ideal gas BEC transition temperature

$$T_c = \frac{3.3\,\hbar^2}{m\,k_B}\left(\frac{n}{g}\right)^{2/3}$$

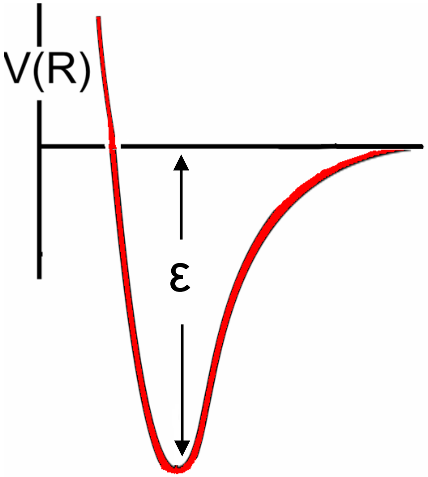
$$T_c(pH_2) = 6.0\ K$$

Parameters

Hydrogen is More Strongly Bound and Less Delocalized than Helium



	He	H_2
R_m [Å]	3.0	3.44
ε [K]	11.0	34.2
Particle vol.[Å^3]	28.9	38.2
Λ*	2.9	2.0



Quantum delocalization is given by the **de Boer parameter**

$$\Lambda^* = \frac{\lambda(\varepsilon)}{R_m} \quad \text{where} \quad \lambda(\varepsilon) = \frac{h}{\sqrt{m\varepsilon}}$$

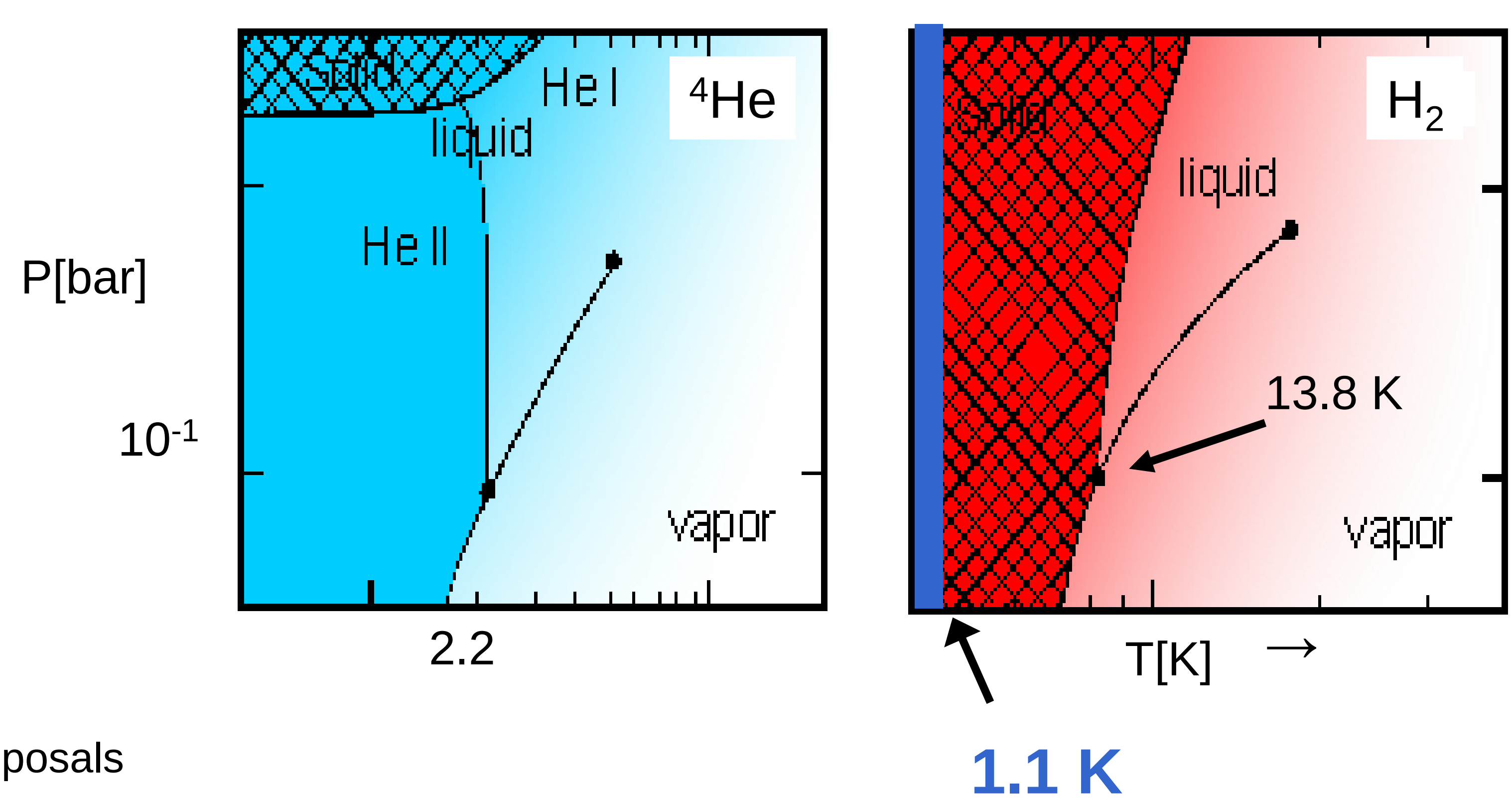
Phase diagram

The Superfluid transition temperature is estimated to be only

$$T_{SF}(pH_2) \approx 1.1K$$

Apenko, Phys. Rev. B60, 3052 (1999)

The Problem with Hydrogen is that it Solidifies at 13.8 K



proposals

Methods Proposed for Creating Superfluid H_2

Depression of melting point by going to negative pressures	Theory
Depression of Debye temperature by adding impurities	Theory
Supercooling drops inside liquid ^{4}He	Expt.
Depression of melting point in porous Vycor glass	Expt.
Supercooling droplets in free jet expansions	Expt.
Forced liquid-solid phase equilibrium	Theory
Forced cooling of a microfilament of liquid	Expt.
Small clusters	Theory and Expt.

outline

Methods Proposed for Creating Bulk Superfluid H_2

Depression of melting point by going to negative pressures	Theory	Ginzburg and Sobyanin, **1972**
Depression of Debye temperature by adding impurities	Theory	Gelikman, 1974
Supercooling drops inside liquid ^{4}He	Expt.	Maris et al., 1983 – 87
Depression of melting point in porous Vycor glass	Expt.	Torii, Maris and Seidel, 1990
Supercooling droplets in free jet expansions	Expt.	Knuth, Schünemann and Toennies, 1995
Forced liquid-solid phase equilibrium	Theory	Vorob'ev and Malyshenko, 2000
Forced cooling of a microfilament of liquid	Expt.	Grisenti et al., 2006
Small clusters	Theory	Ceperley et al, 1991

Vorobev

Outline

I. Introduction: BEC and Superfluidity

II. Theory of Small para-H_2 (pH_2) Clusters

III. Raman Spectroscopy of Pure pH_2 clusters

IV. Matter-Wave Diffraction of H_2 Clusters

V. Spectroscopic Evidence for Superfluidity

Experimentalists	Theoreticians
Andrej Vilesov , now USC	David Ceperley, Illinois
Slava Grebenev, now Kirov	Boris Sartakov, Moscow
Anton Kalinin, Göttingen	Mikhail Sevryuk, Moscow
Oleg Kornilov, now Berkeley	

PIMC

Path Integral Monte Carlo Method I

Partition Function $Z(\beta) = Trace\ \exp(-\beta H) = \int dR\, \rho(R, R; \beta)$

where $\beta = 1/kT$ and $\rho(R, R; \beta)$ is the position space density matrix.

It is a function of the 3N coordinates of all the particles.

Via a convolution theorem it can be decomposed into M segments

which is reptresented by an integral over a path with time steps $\tau = \beta / M$

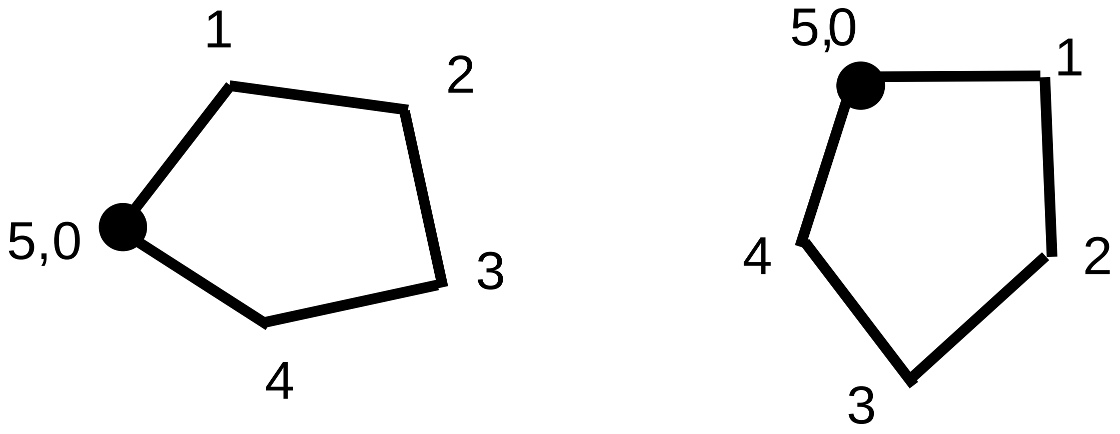
$$\rho(R_0, R_M; \beta) = \int \ldots \int dR_1\, dR_2 \ldots dR_{M-1}\, \rho(R_0, R_1; \tau)\, \rho(R_1, R_2; \tau) \ldots \rho(R_{M-1}, R_M; \tau)$$

The path for each particle is called a *polymer* and consists of „beads“ and the beads in the different polymers are coupled by the intermolecular potential.

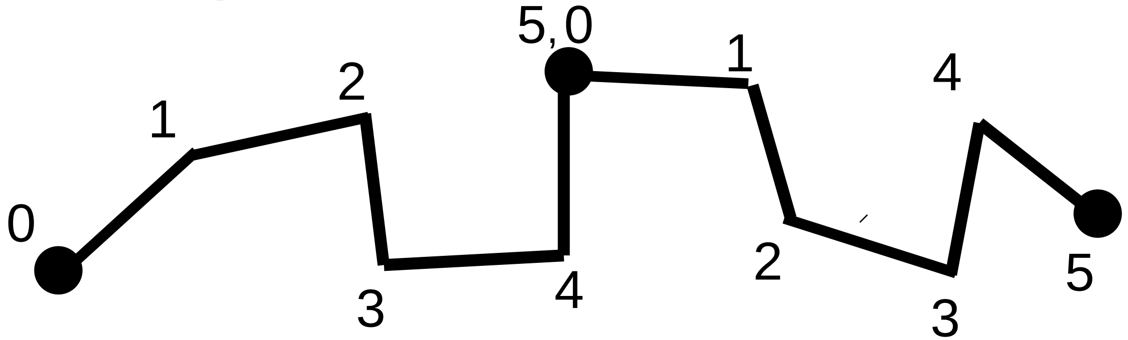
Path Integral Monte Carlo Method II

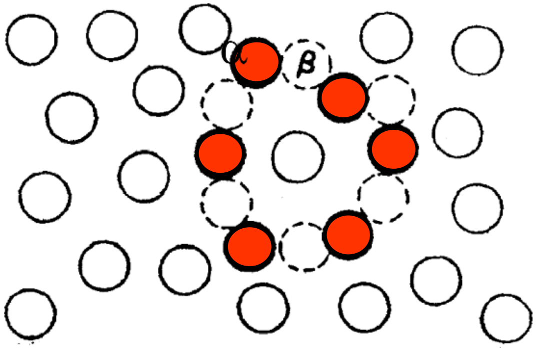
The size L of each polymer is $L \approx \lambda$

$T > T_C$ $\lambda < l$ separate „polymers“



$T < T_C$ $\lambda \approx l$ linked „polymers“allow for bose exchange



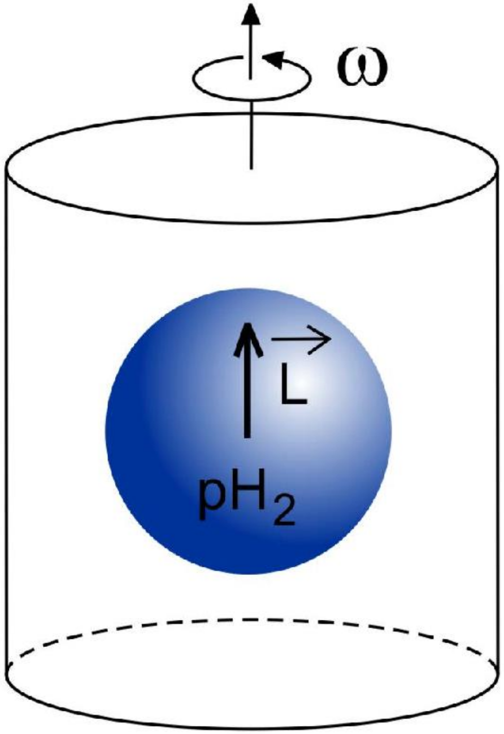


The trajectories are then used to calculate the partition function

Evaluation of Superfluid Response to Rotations: Non-Classical Rotational Moment of Inertia I

Slow rotation of external field with frequency $\vec{\omega}$

$$I_{ij} = \left.\frac{\partial < L_i >}{\partial \omega_j}\right|_{\omega = 0} = I_{ij}^{cl} - \frac{4m^2 < A_i A_j >}{\beta \hbar^2}$$



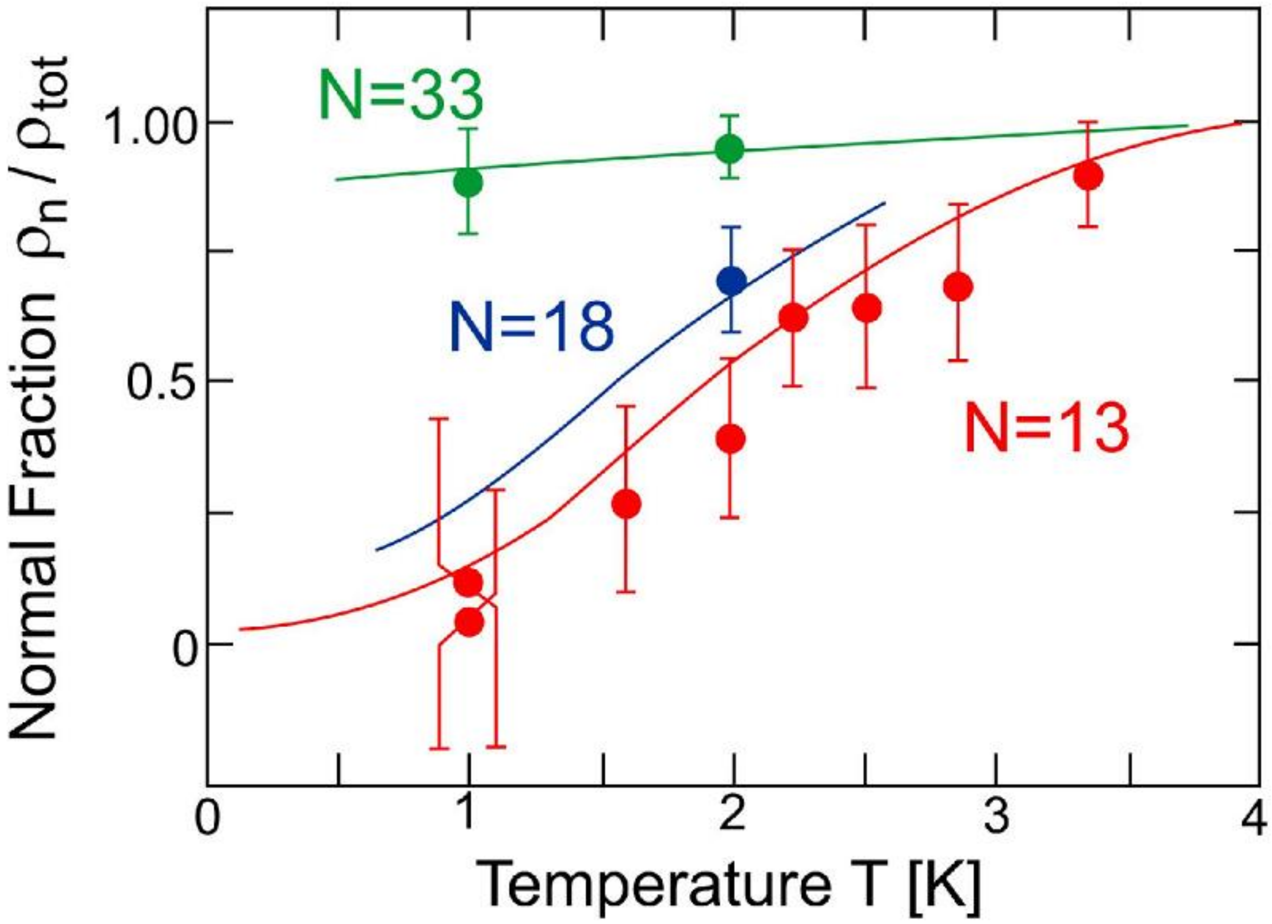
$A_i =$ area of Feynman path projected onto axis i

$$I^{cl}{}_{ij} = m \int d\vec{r} \rho(\vec{r})(r^2 \delta_{ij} - x_i x_j)$$

$$f_\alpha^s = 1 - \frac{I_\alpha}{I_\alpha^{cl}} = \frac{4m^2 \left\langle A_\alpha^2 \right\rangle}{\beta \hbar^2 I_\alpha^{cl}}$$

Sindzingre, Klein, and Ceperley,: Phys. Rev. Lett. 67, 1871 (1991)

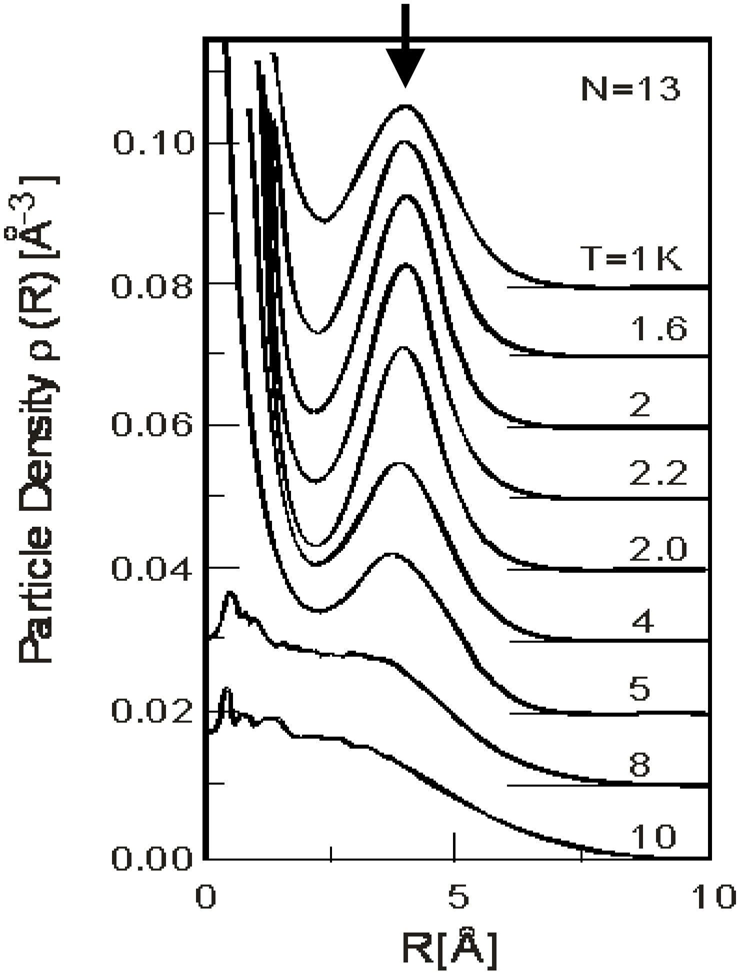
The Reduced Coordination In Small Droplets Favors Superfluid Response



Sindzingre, Klein, and Ceperley,: Phys. Rev. Lett. 67, 1871 (1991)

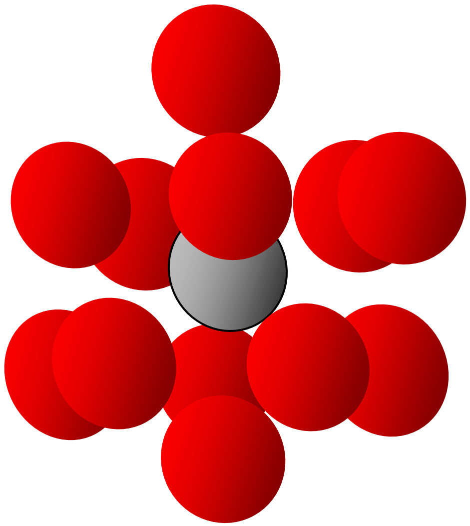
Density dist

The PIMC Calculated Radial Density Distributions Suggest a „Rigid“-Like Structure



Thermal Melting →

Classical $(p\text{-}H_2)_{13}$ Cluster



N=13 Icosahedral Structure

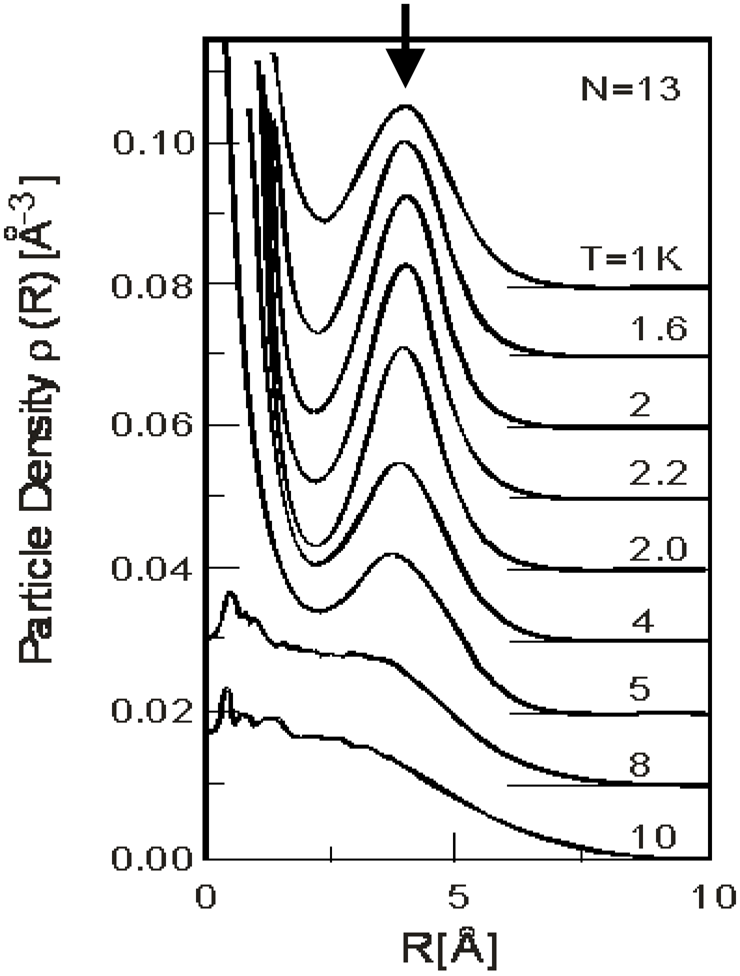
Sindzingre, Klein, and Ceperley,

Srructure

H_2: Phys. Rev. Lett. 67, 1871 (1991) ^{4}He: Phys. Rev. Lett. 63 1601 (1989)

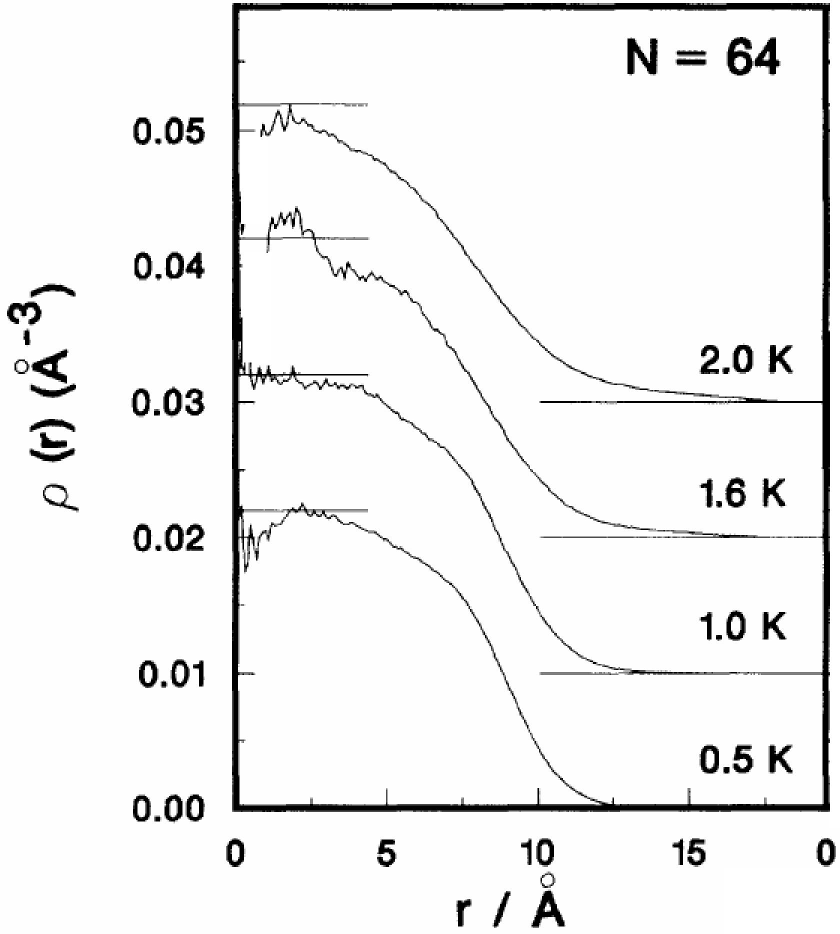
The PIMC Calculated Radial Density Distributions Suggest a „Rigid“-Like Structure

p-H_2 Cluster



Thermal Melting ⟶

Superfluid ^{4}He Cluster



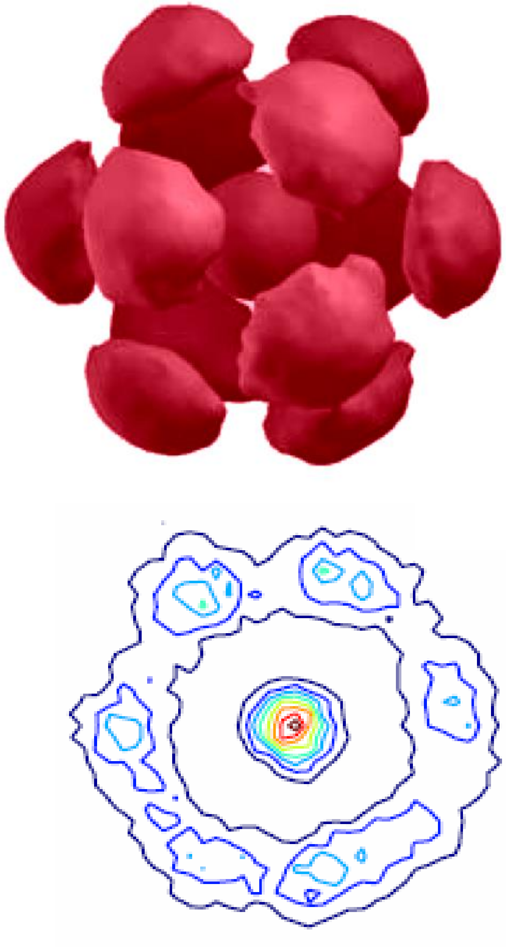
Sindzingre, Klein, and Ceperley,

Srructure

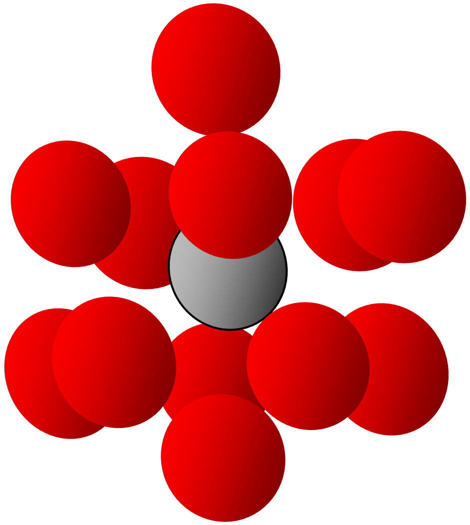
H_2: Phys. Rev. Lett. 67, 1871 (1991) ^{4}He: Phys. Rev. Lett. 63 1601 (1989)

Structure of a $(p\text{-}H_2)_{13}$ Cluster

Quantum Mechanical



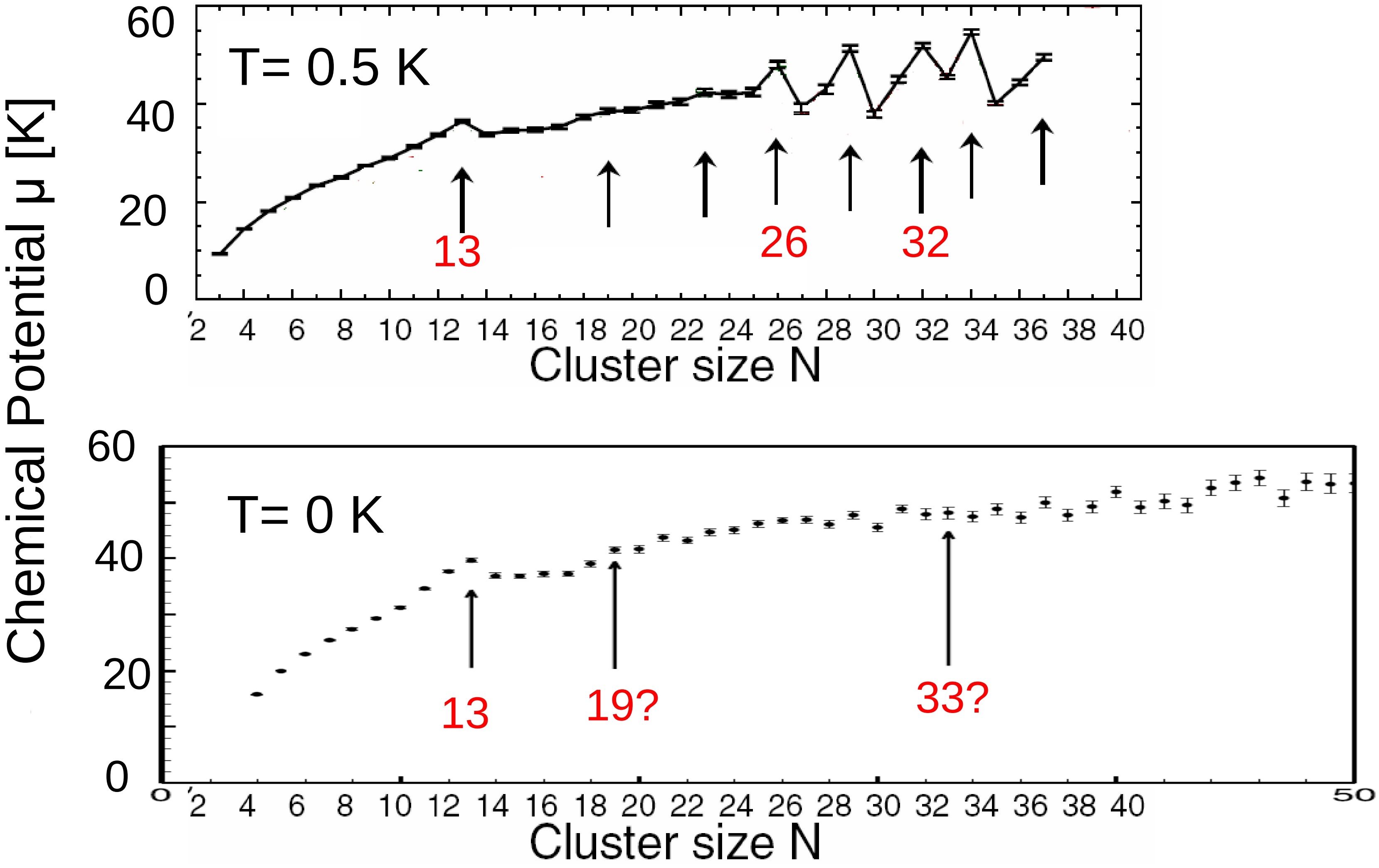
Classical



N=13 Icosahedral Structure

Magic nos

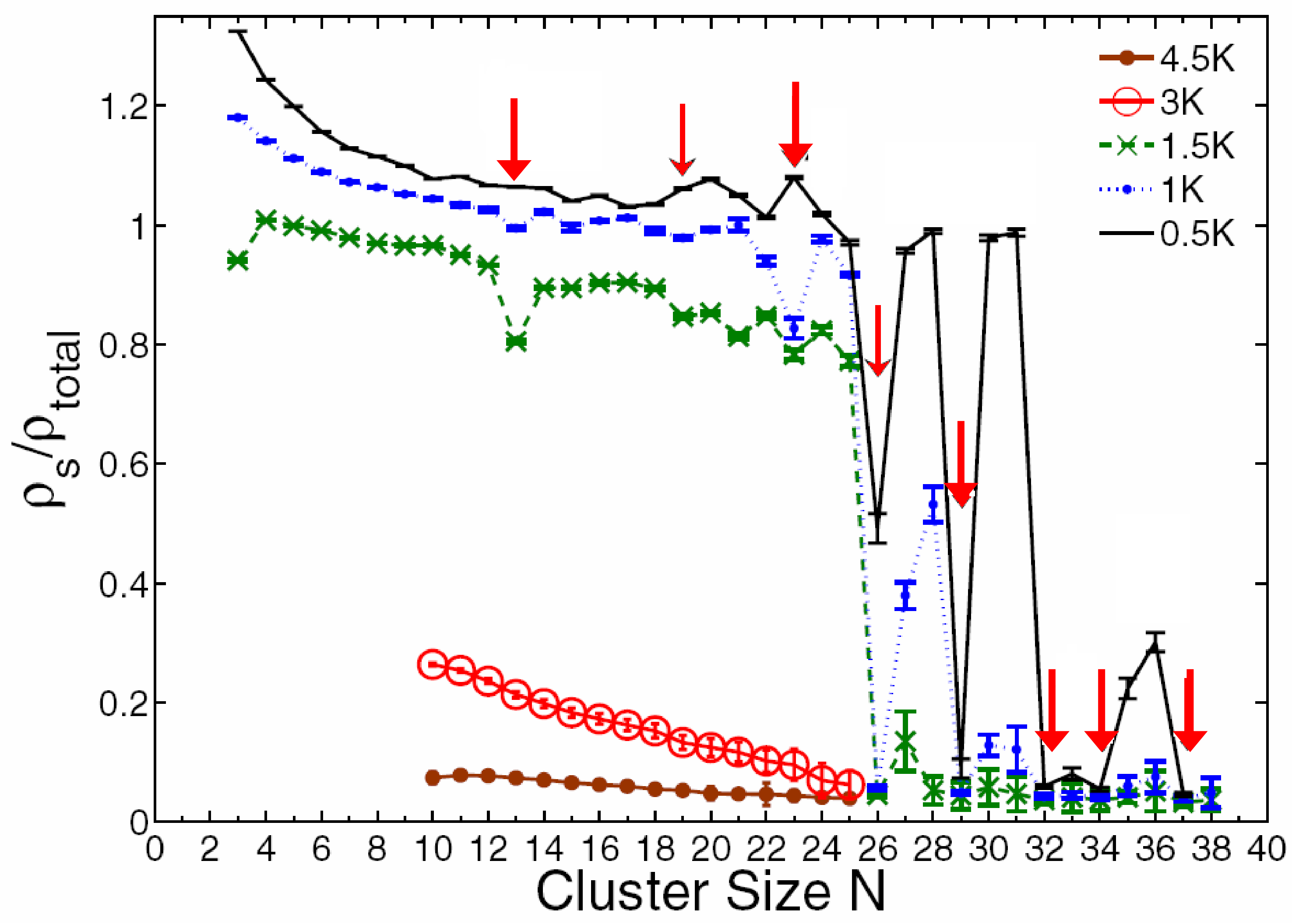
The Chemical Potential (μ=ΔE/ΔN) Reveals Magic Stabilities



Is the Disappearance at T=0 due to Quantum Melting??

PIMC: Khairallah et al, Phys. Rev. Lett. 98, 183401 (2007). DMC: Navarro and Guardiola, JLTP 148, 857 (2007)

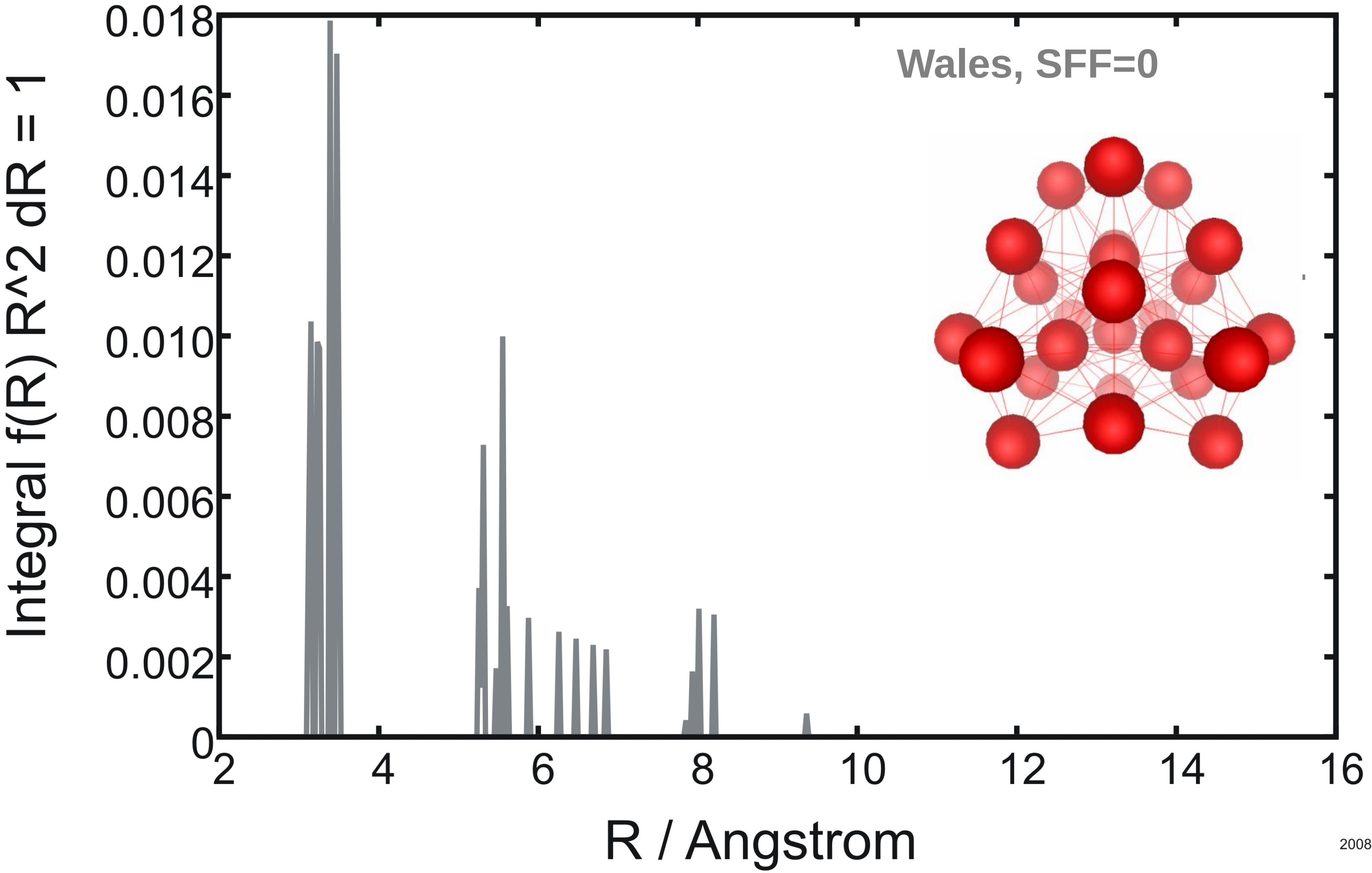
The Superfluid Fraction is Depressed at the Magic Numbers



Khairallah, Sevryuk, Ceperley and Toenniesl, Phys. Rev. Lett. 98, 183401 (2007).

Var pot

By Varying the Potential Well Depth Can Study Transition from Solid to Liquid Cluster (N=26,T=0.5K). Call this „Potential“ Melting

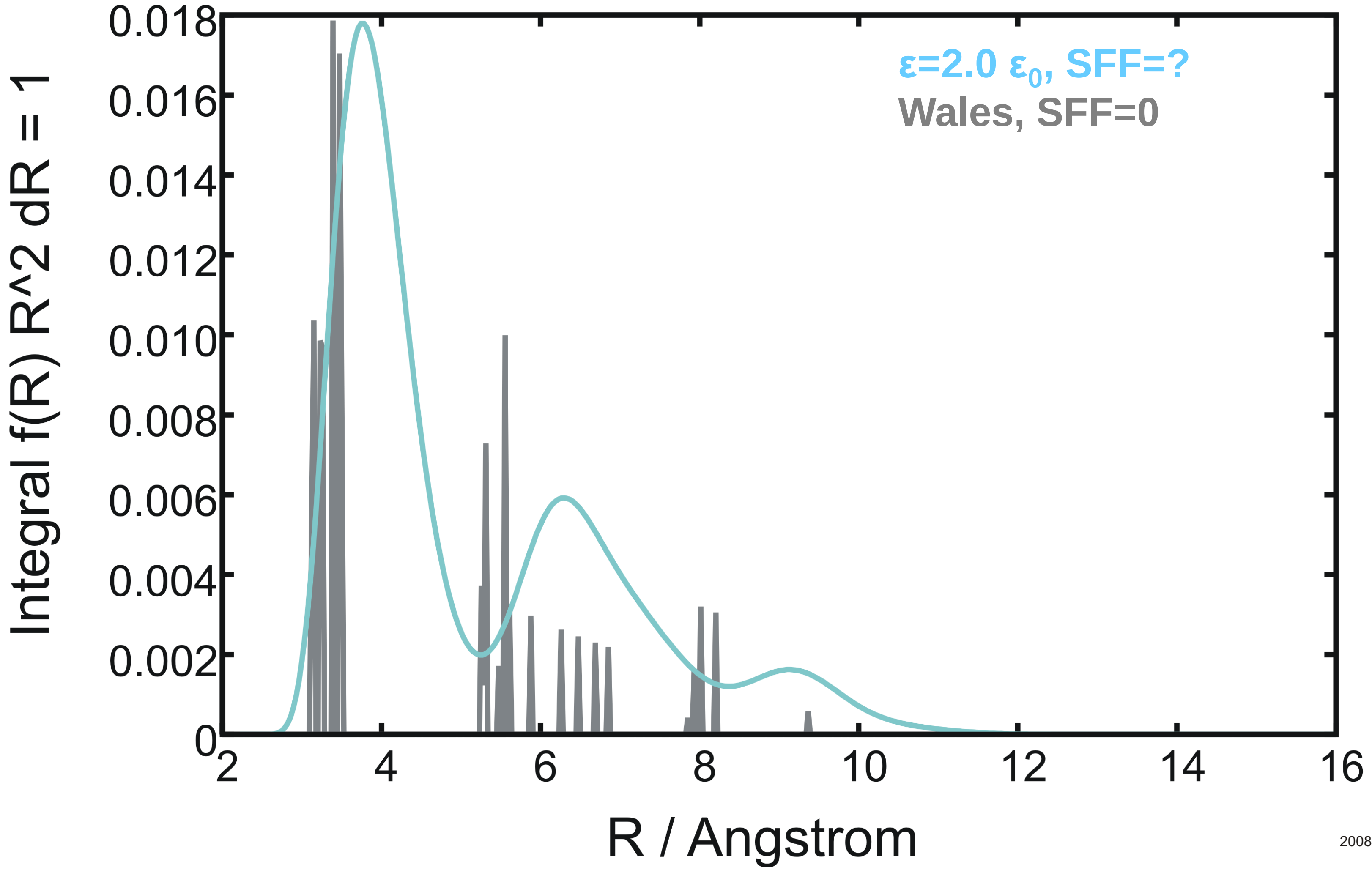


2008-08-13-T2-Wa

Ceperley, Sevryuk and Toennies, in progress

Radial density profiles f for para-clusters: N = 26 at T = 0.5 K

Various epsilons (34.2 K is the "true" one); the Wales structure scale is arbitrary



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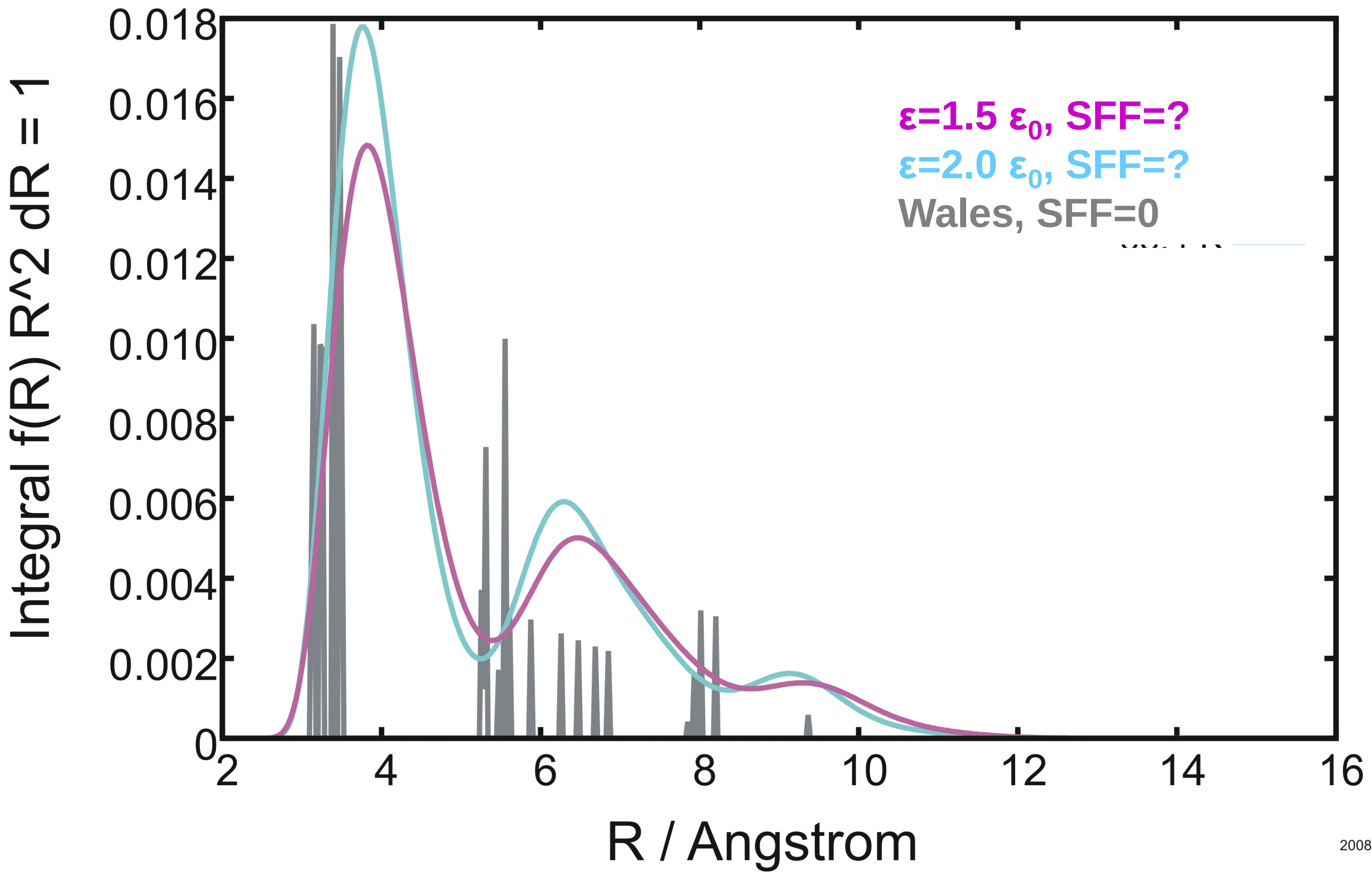

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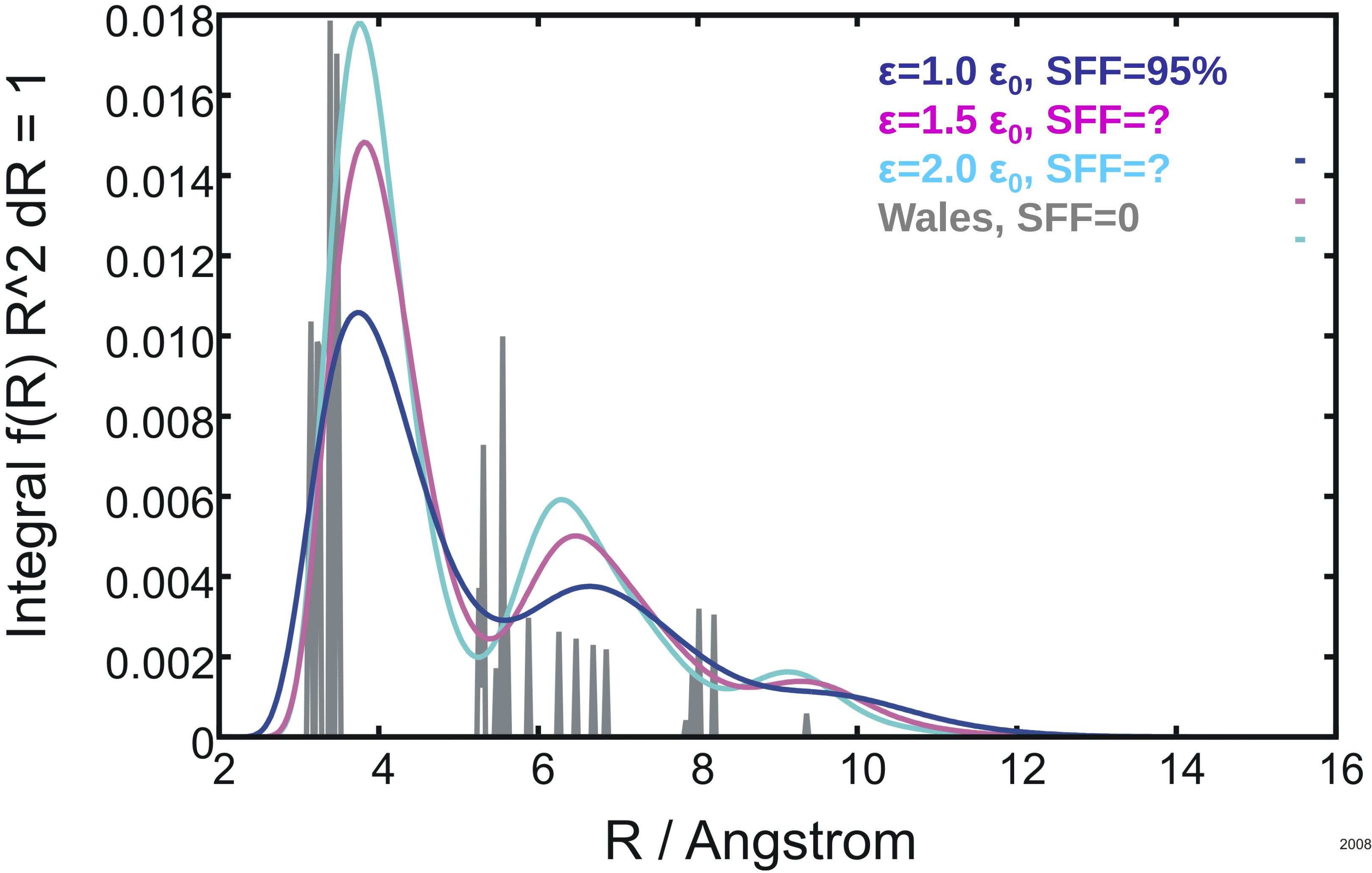

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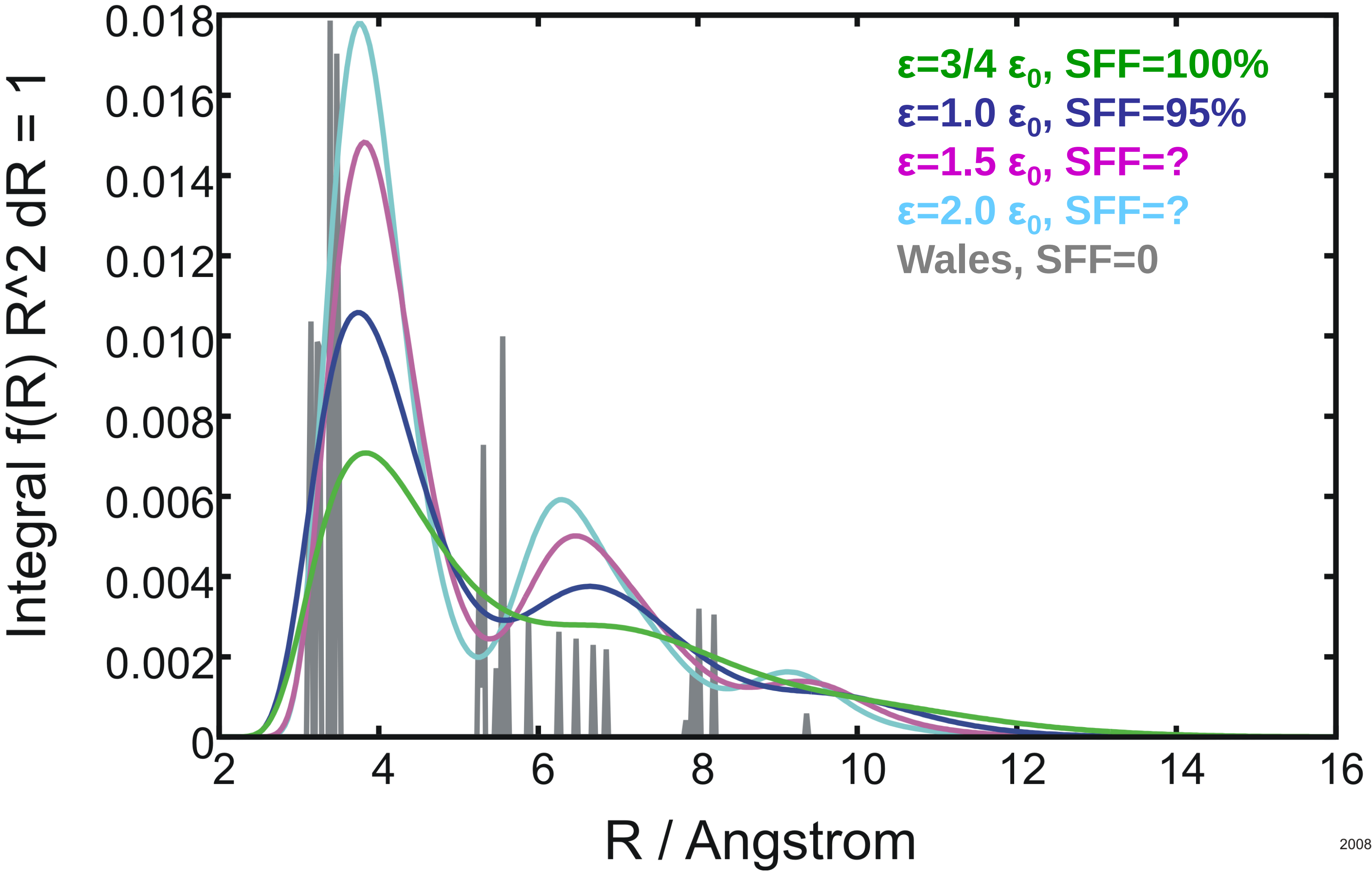

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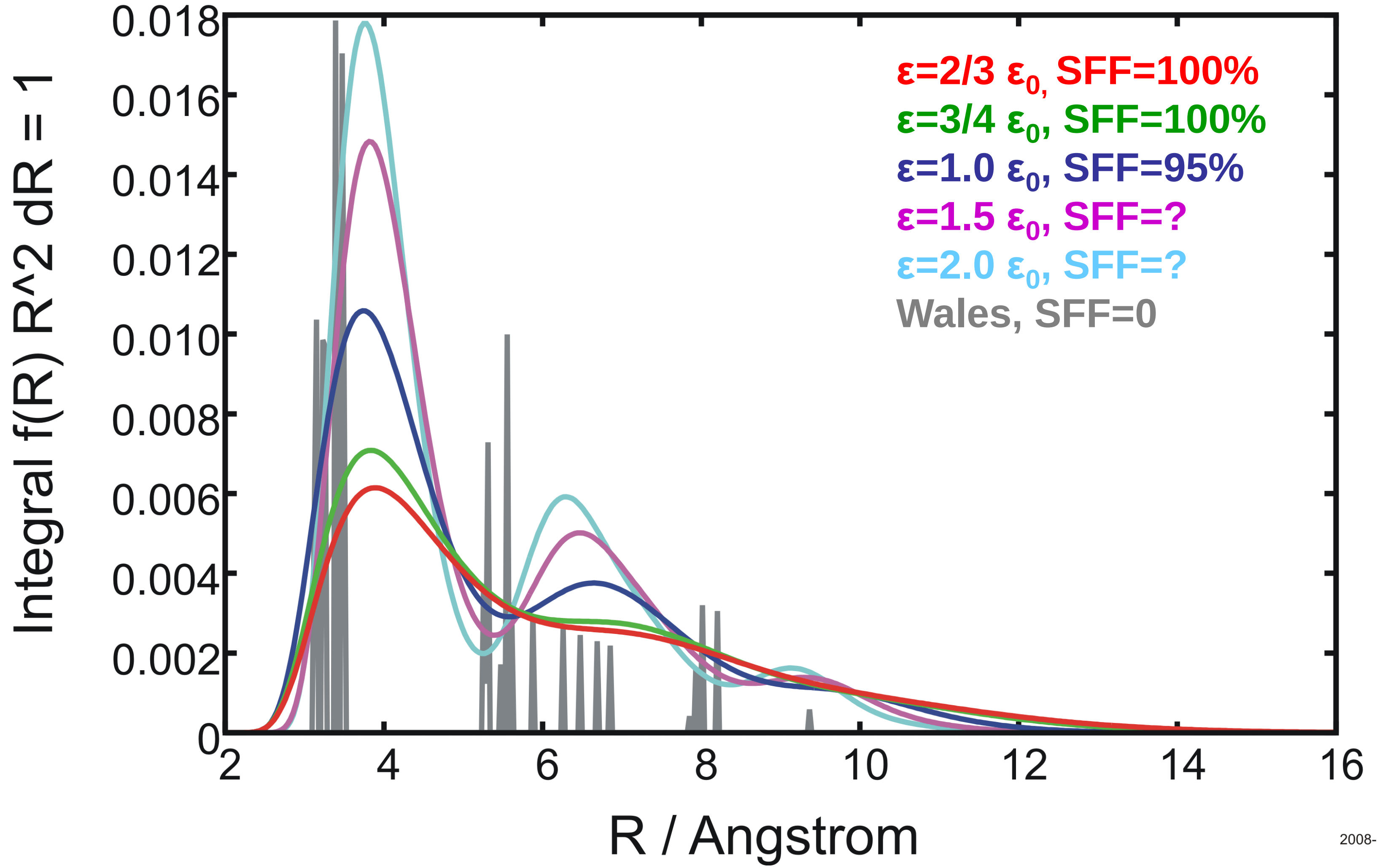

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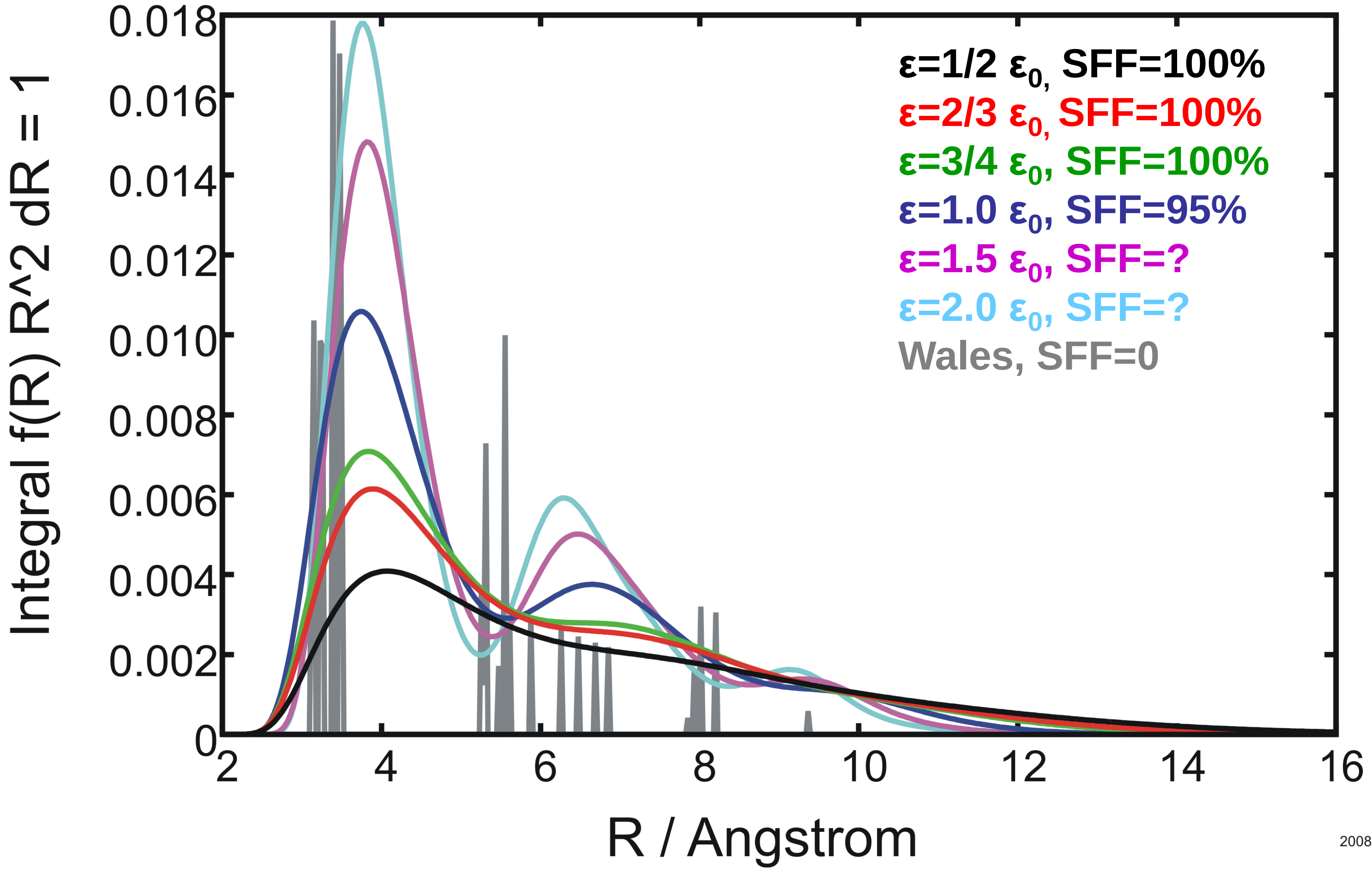
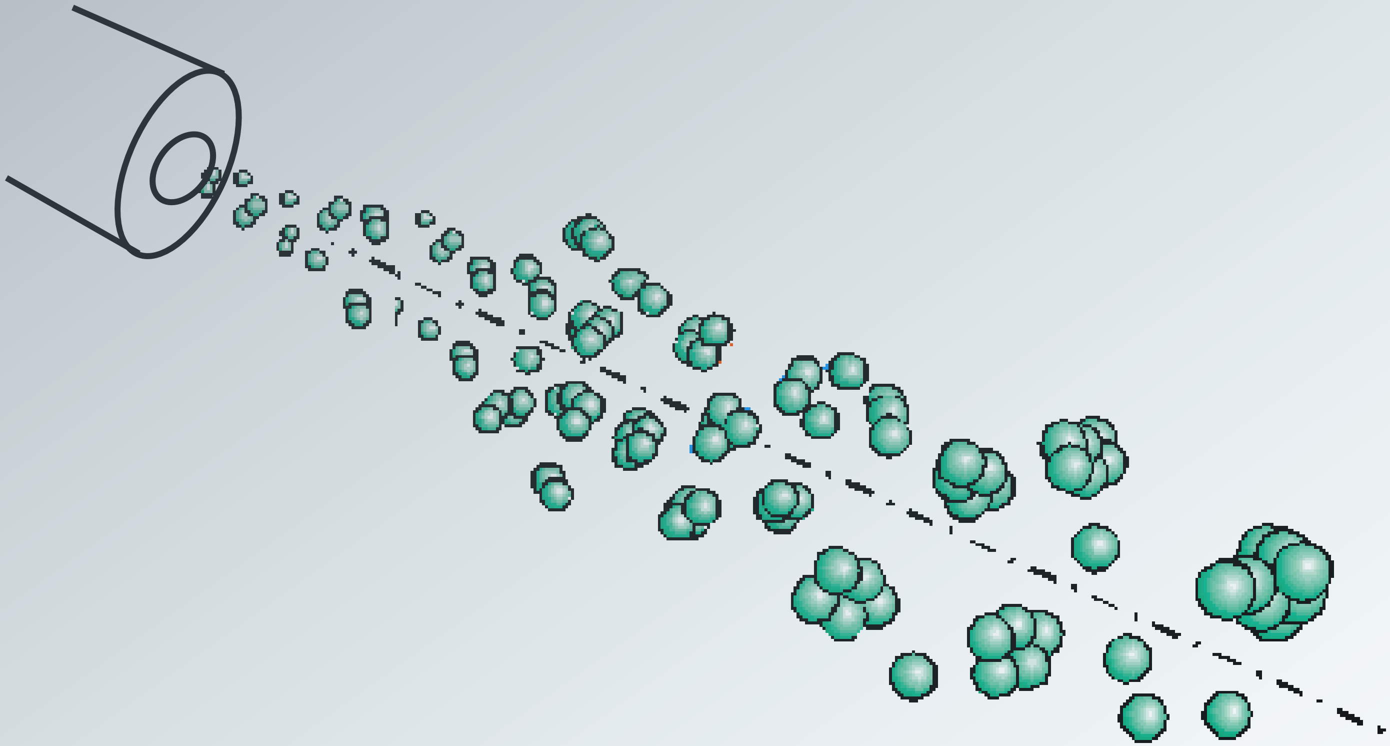


2008-08-13-T2-Wa

CI expts

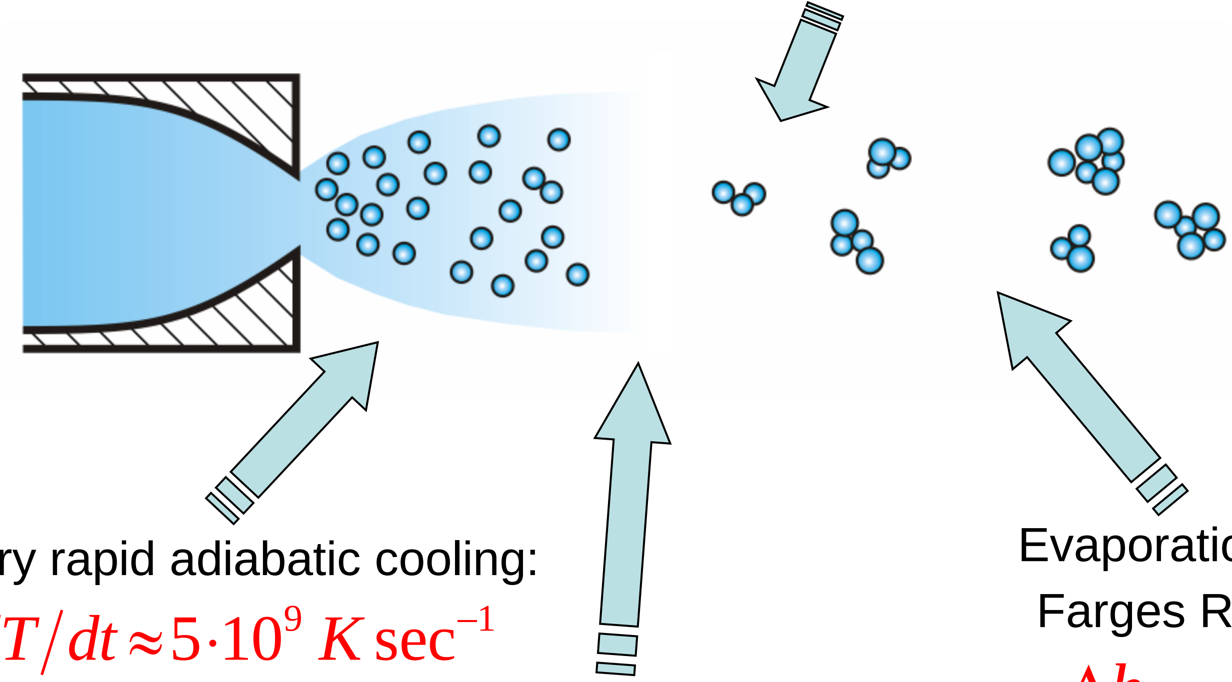
Clusters Experiments



Free Jet Expansions Provide Most Rapid Cooling and Low Evaporation Temperatures

Hetero-nucleation minimized:
purity of gas < 10^{-4} ⟶
much less than 1 impurity per cluster

T_0=20 K, P_0=1 bar



By seeding in He ambient temperatures can be reduced to 0.1 - 0.5 K

Very rapid adiabatic cooling:

$$dT/dt \approx 5 \cdot 10^9\ K\,\mathrm{sec}^{-1}$$

Melting point is reduced in small droplets

$$T_m/T_{tp} = 1 - \exp(-0.11\,\ell n\, N)$$

$$\approx 0.64\ (N = 10^4)$$

Evaporation cooling

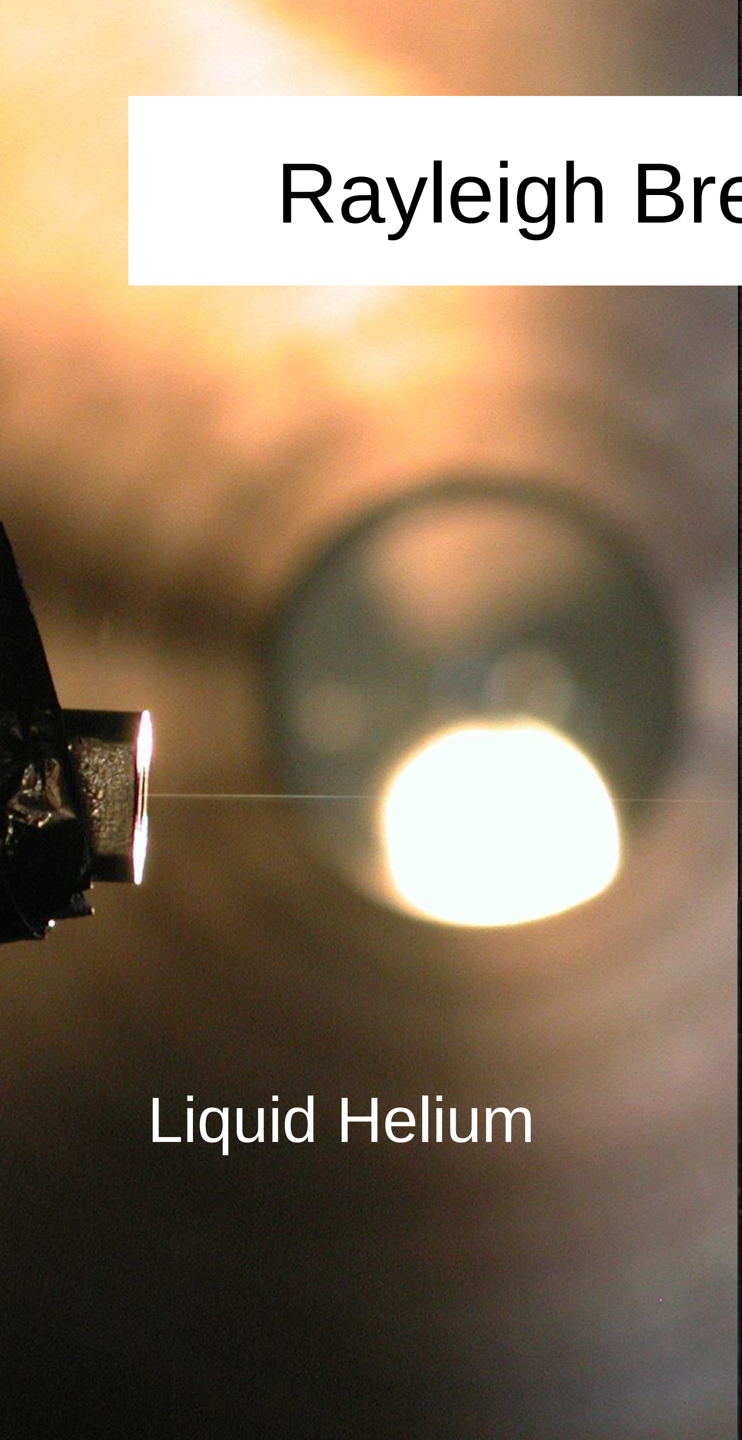
Farges Rule: $T_\infty \propto \Delta h_{evap}$

$$\Delta h_{evap}(H_2) = 109\,K,$$

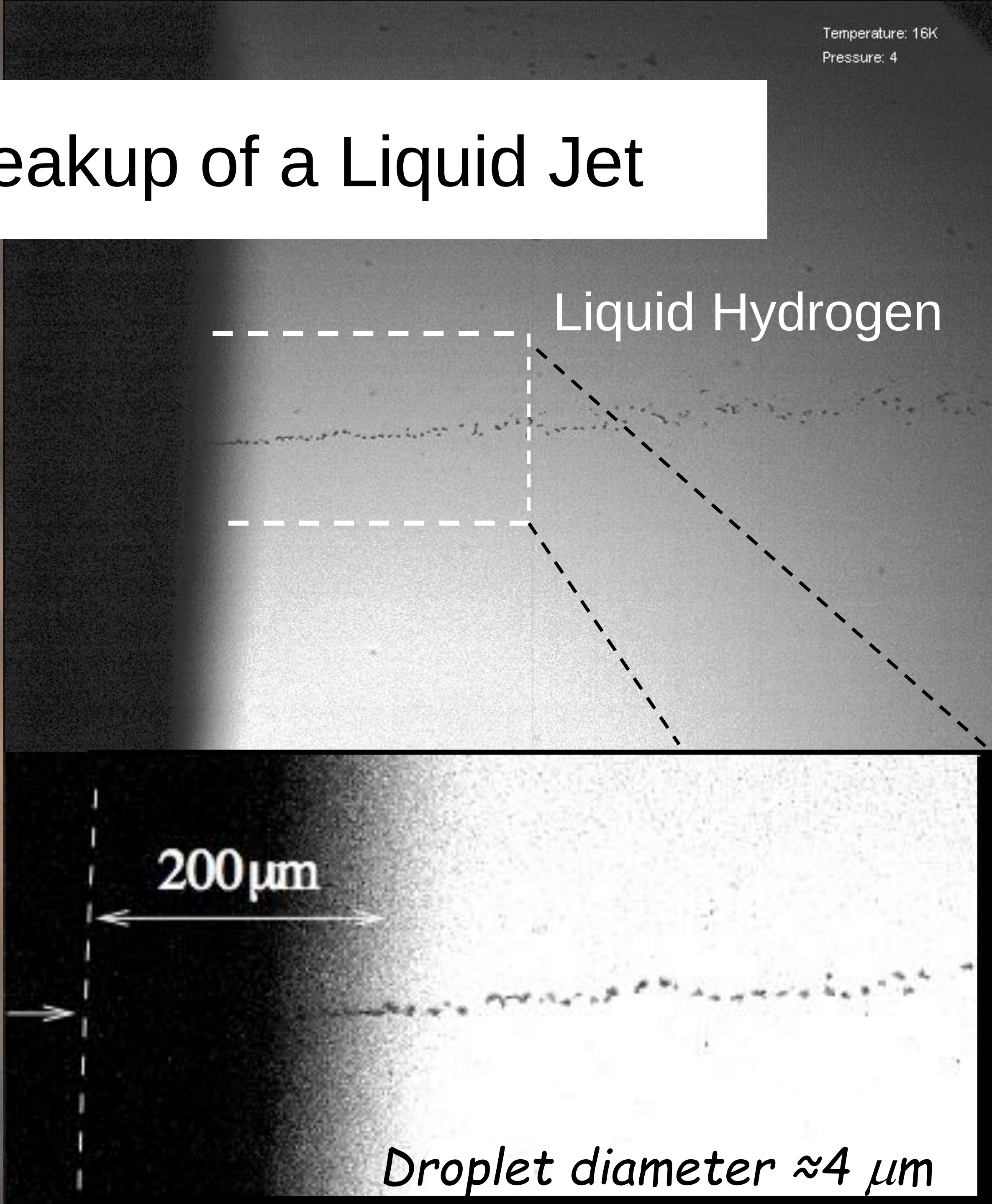
$$T_\infty = 5.75\,K\ (4.5\,K)$$

photos

Rayleigh Breakup of a Liquid Jet



Liquid Helium



Liquid Hydrogen

Droplet diameter ≈4 μm

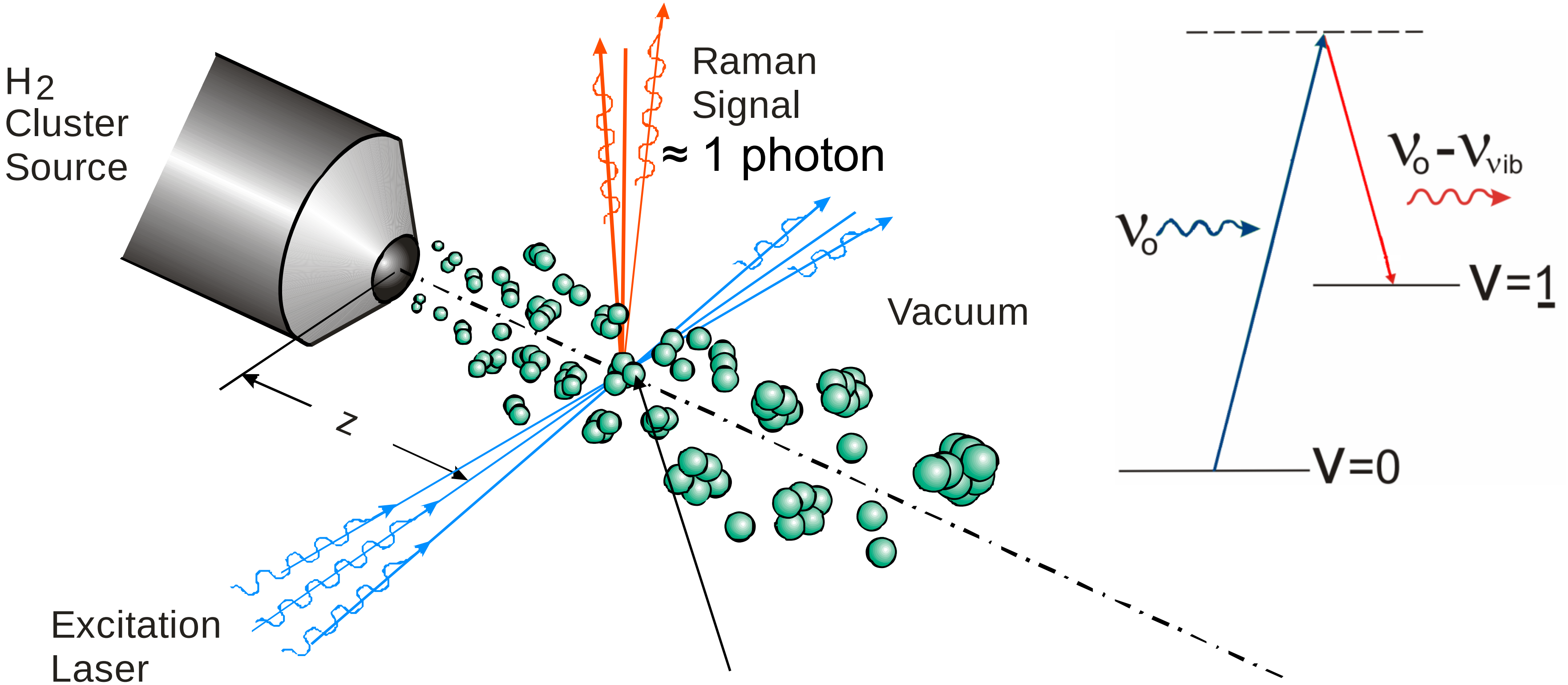
Detection of H_2 Clusters is Problematic

- Spectroscopies
  - ~~Neutron scattering~~
  - ~~Electron scattering~~
  - ~~X-ray scattering~~
  - ~~UV absorption~~
  - ~~Infra-red~~
  - Raman scattering

- Others
  - ~~Mass spectroscopy~~
  - Matter-wave diffraction

Montero

Raman „Microscopic“ Spectroscopy Inside Free Jet Expansions: Small Clusters of p-H_2



H_2 Cluster Source

Raman Signal

≈ 1 photon

Vacuum

z

ν_o

$\nu_o - \nu_{vib}$

$V=\underline{1}$

$V=0$

Excitation Laser

$\lambda = 514.5$ nm (4W)

10^{20} photons

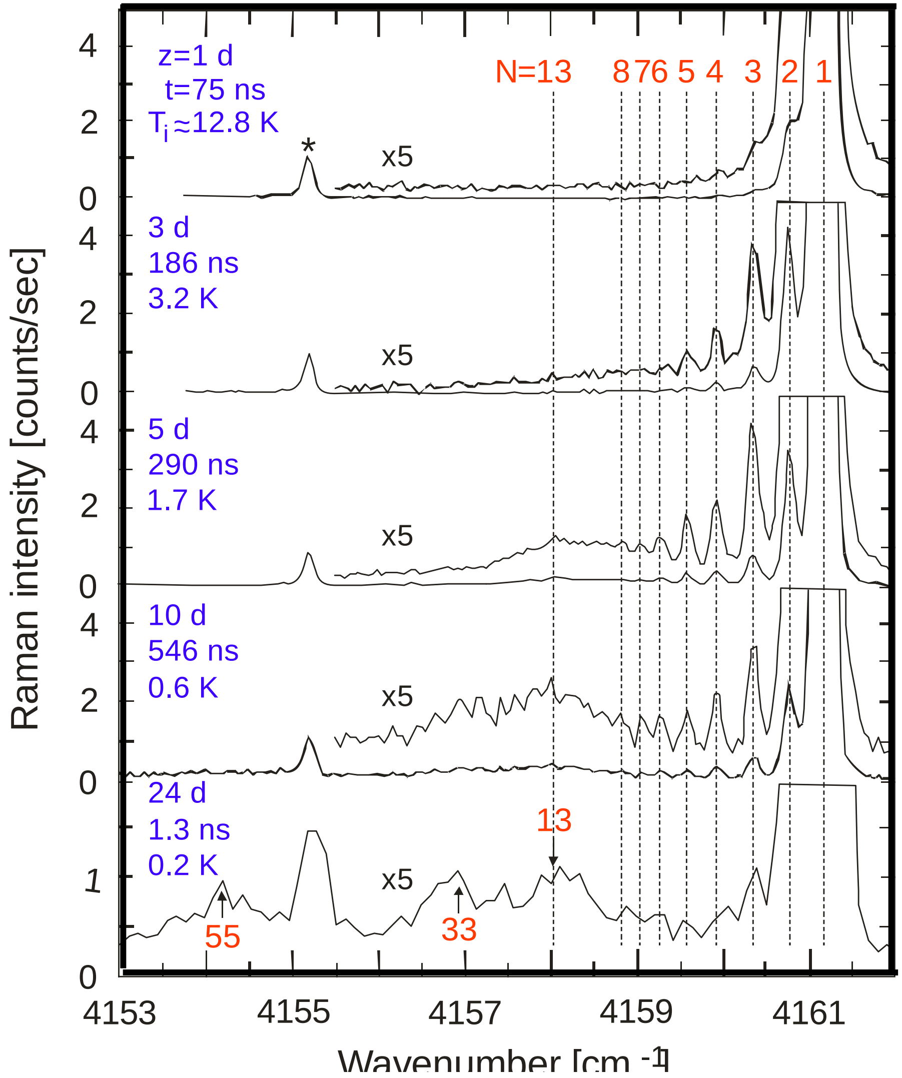
2x2x2 micron

2004-04-19-T4-Ba

Spectra

Tejeda, Fernandez, Montero, Blume and Toennies, Phys. Rev. Lett. <u>92</u>, 223401 (2004)

Magic Numbers Appear in High Resolution Raman Spectra of (pH_2) Clusters with Distance



T_0=46.5 K
P_0=1 bar
d=50 micron

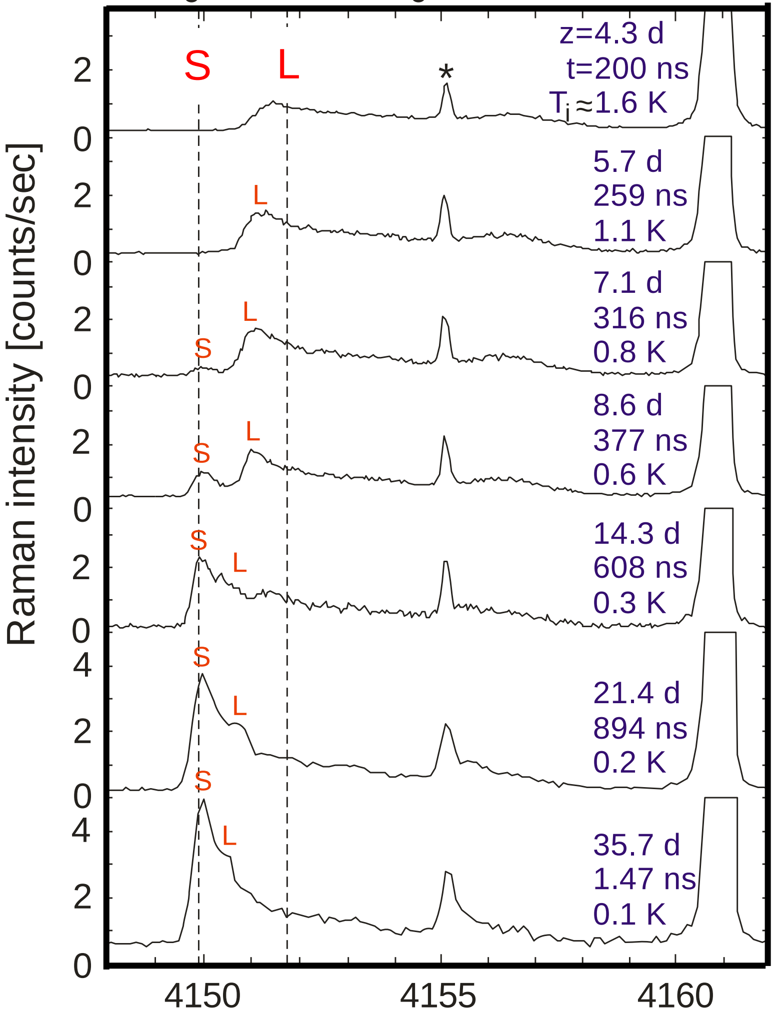
Tejeda, Fernandez, Montero, Blume and Toennies, Phys. Rev. Lett. 92, 223401 (2004)

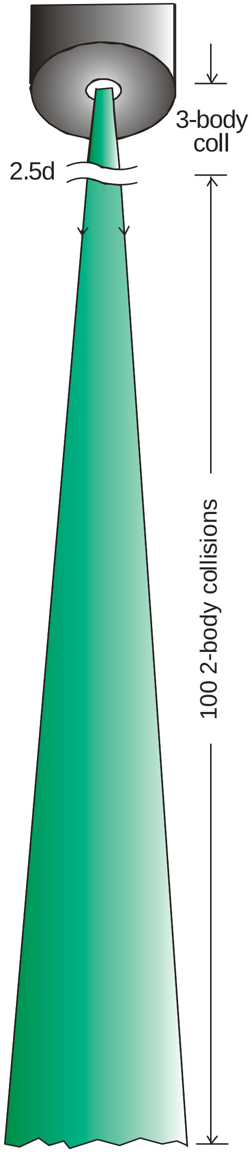
Transition to solid

2004-03-09-T1-Schr.

Evidence for a Liquid - Solid Transition in Large pH_2- Clusters

T_0 =36.5 K, P_0=2 bar, d=35 μ

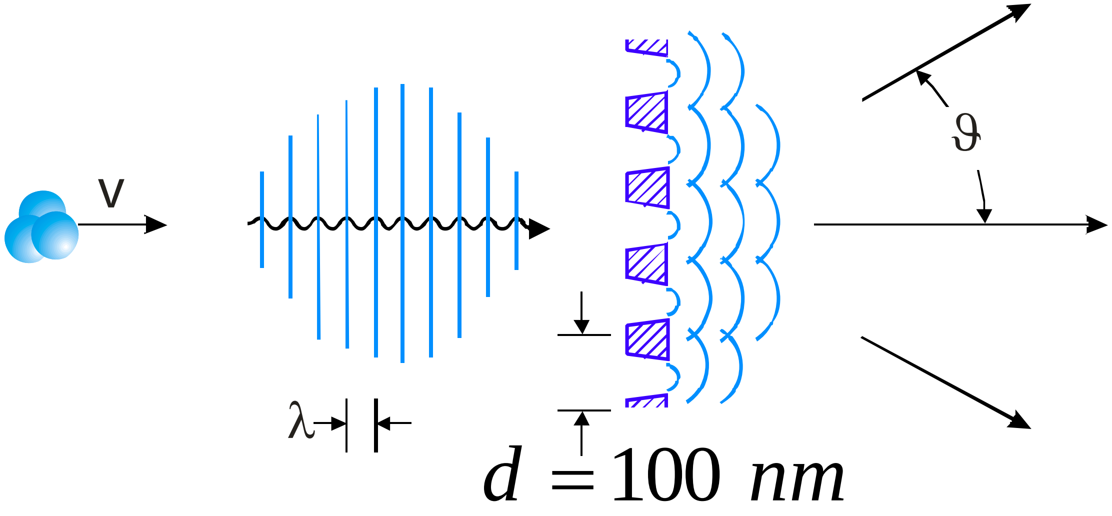




Liquid Clusters also Recently Detected in He Seeded Beams: Kuyanov-Przument and Vilesov, submitted

diffraction

Non-destructive Transmission Grating Diffraction



N-particle Cluster
de Broglie Wavelength

$$\lambda = \frac{h}{N \times (mv)}$$

Diffraction Angles

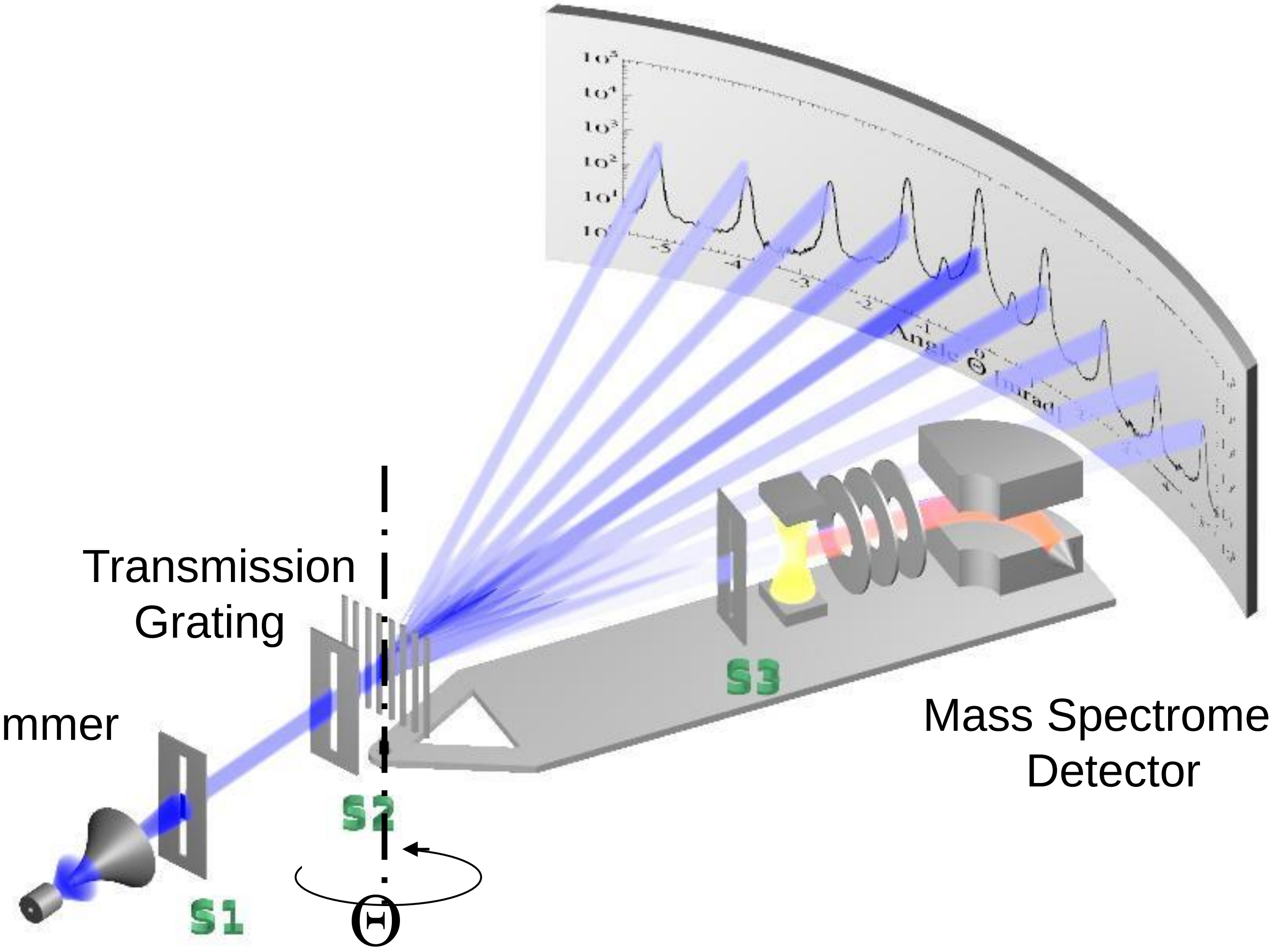
$$\vartheta \approx \frac{\lambda}{d} \quad (n=1)$$

Typically: $\lambda = 0.5\,\text{Å}$, $\vartheta = 0.5\ \text{mrad}$

The diffraction angle is inversely prop. to N

app

Schematic Diagram of the Diffraction Apparatus



Transmission Grating

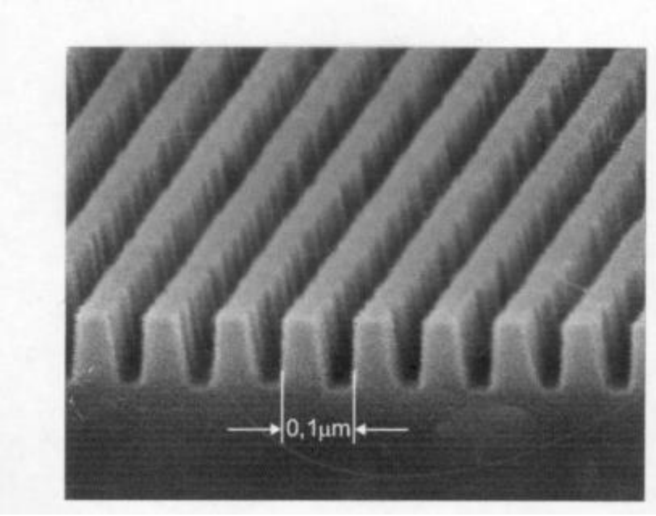
Skimmer

Nozzle

Mass Spectrometer Detector

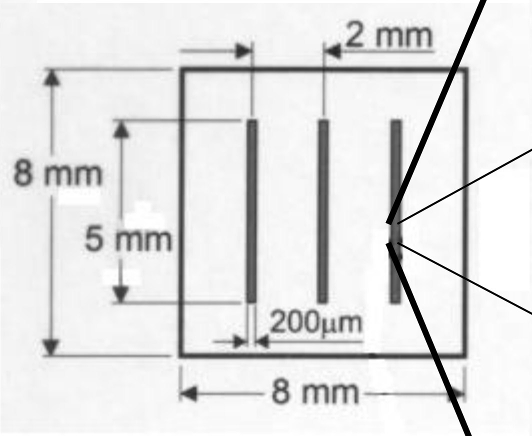
gratings

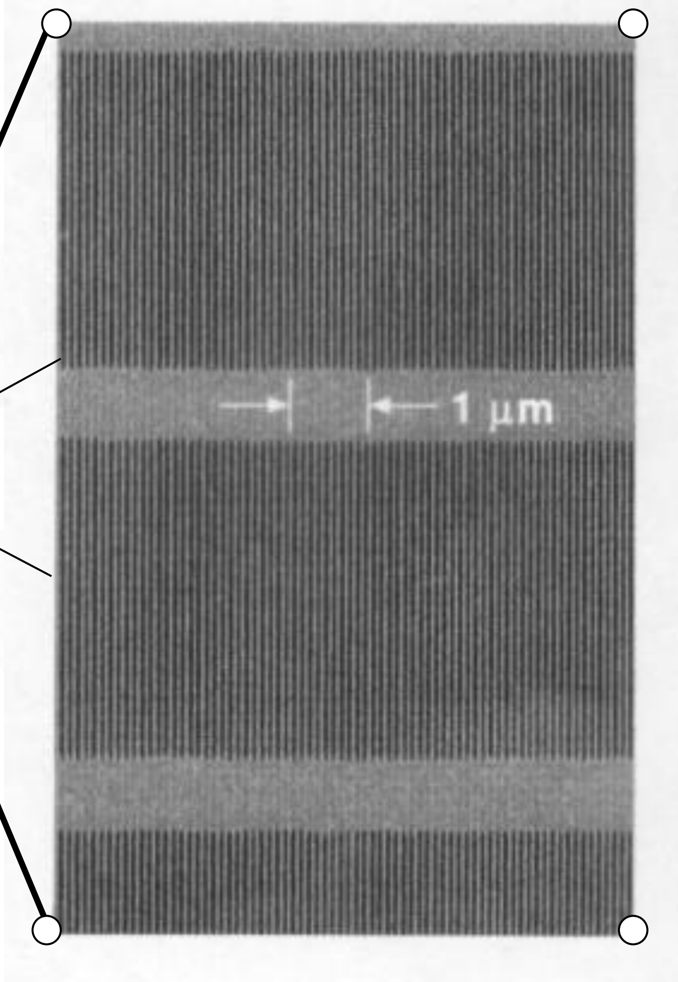
Electron Microscope Picture of the SiN_x Transmission Gratings



View of the chip
before the Si base
is etched away

100 nm period
~50 nm slit width



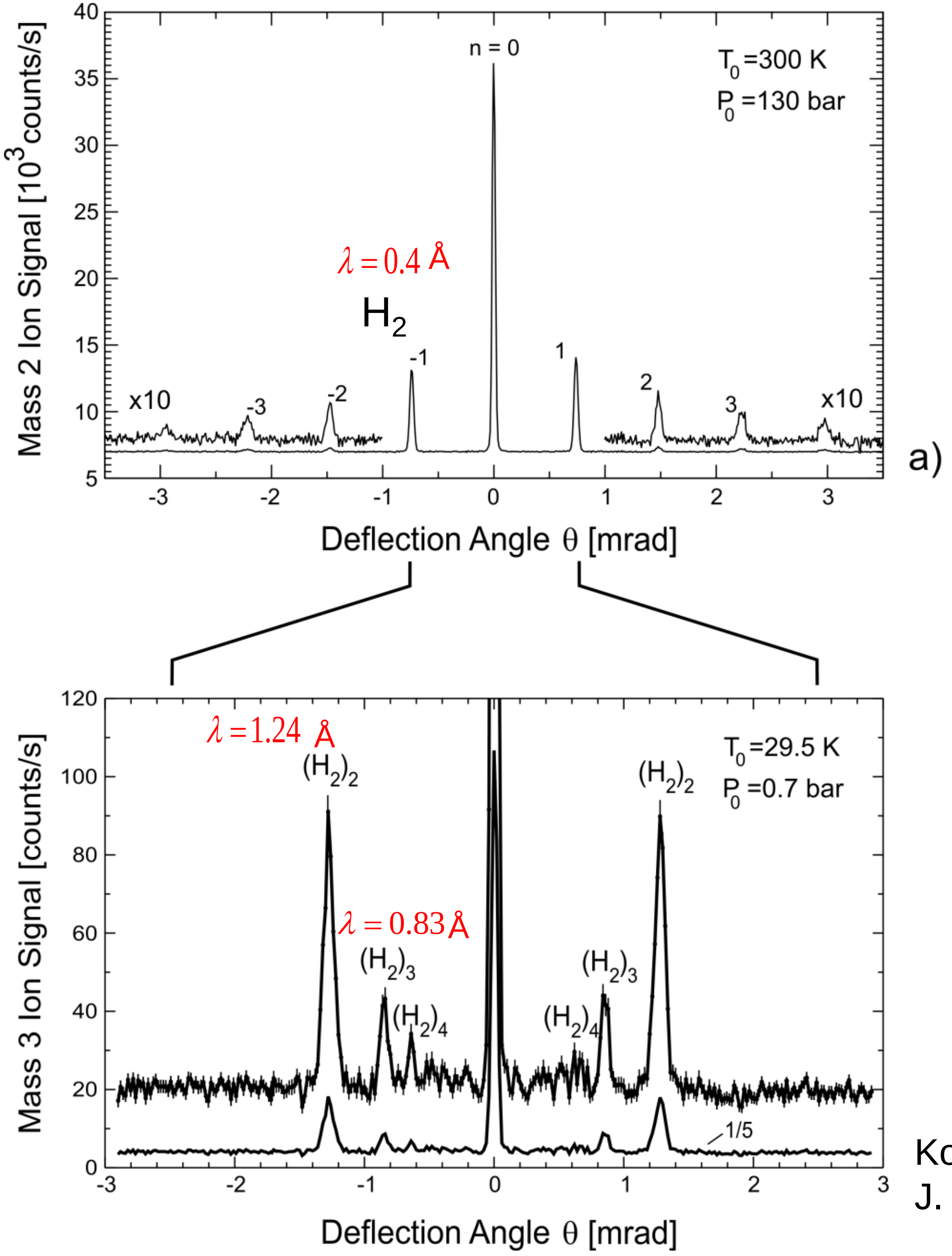


Courtesy of Prof. H. Smith and Dr. Tim Savas ,M. I. T.

Diff patt

Diffraction of Small Normal-H_2 Clusters

P_0 = 130 bar,
T_0 = 300 K



P_0 = 0.7 bar,
T_0 = 29.5 K

ionization

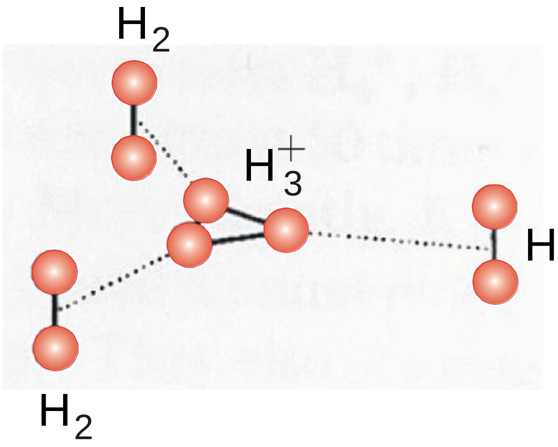
Kornilov and Toennies,
J. Chem.Phys.128,194306 (2008)

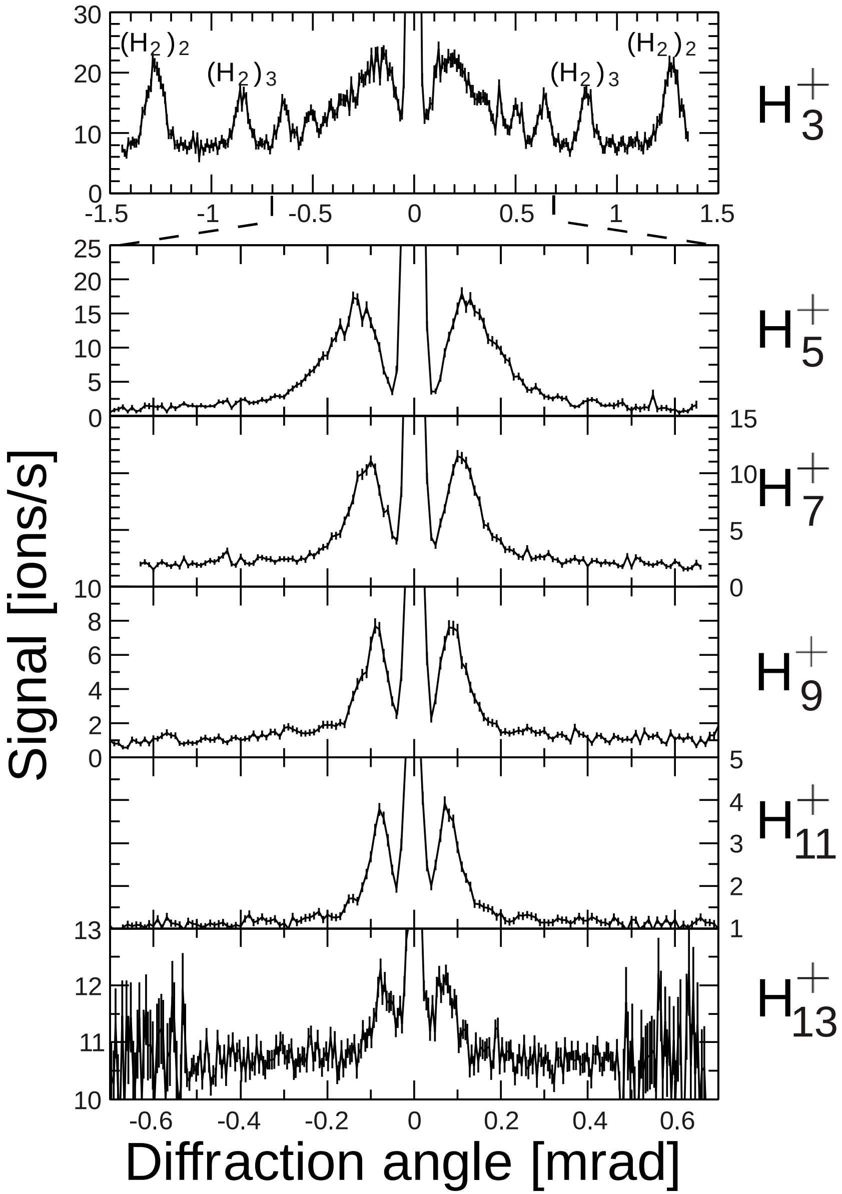
To Obtain the Neutral Cluster Size Distribution Need Fragmentation Pattern: $(H_2)_N + e^- \rightarrow H_K^+ + 2e^-$

Only fragments with odd masses are present:

reaction $H_2^+ + H_2 \rightarrow H_3^+ + H$ has very large cross section.

Structure of ions:

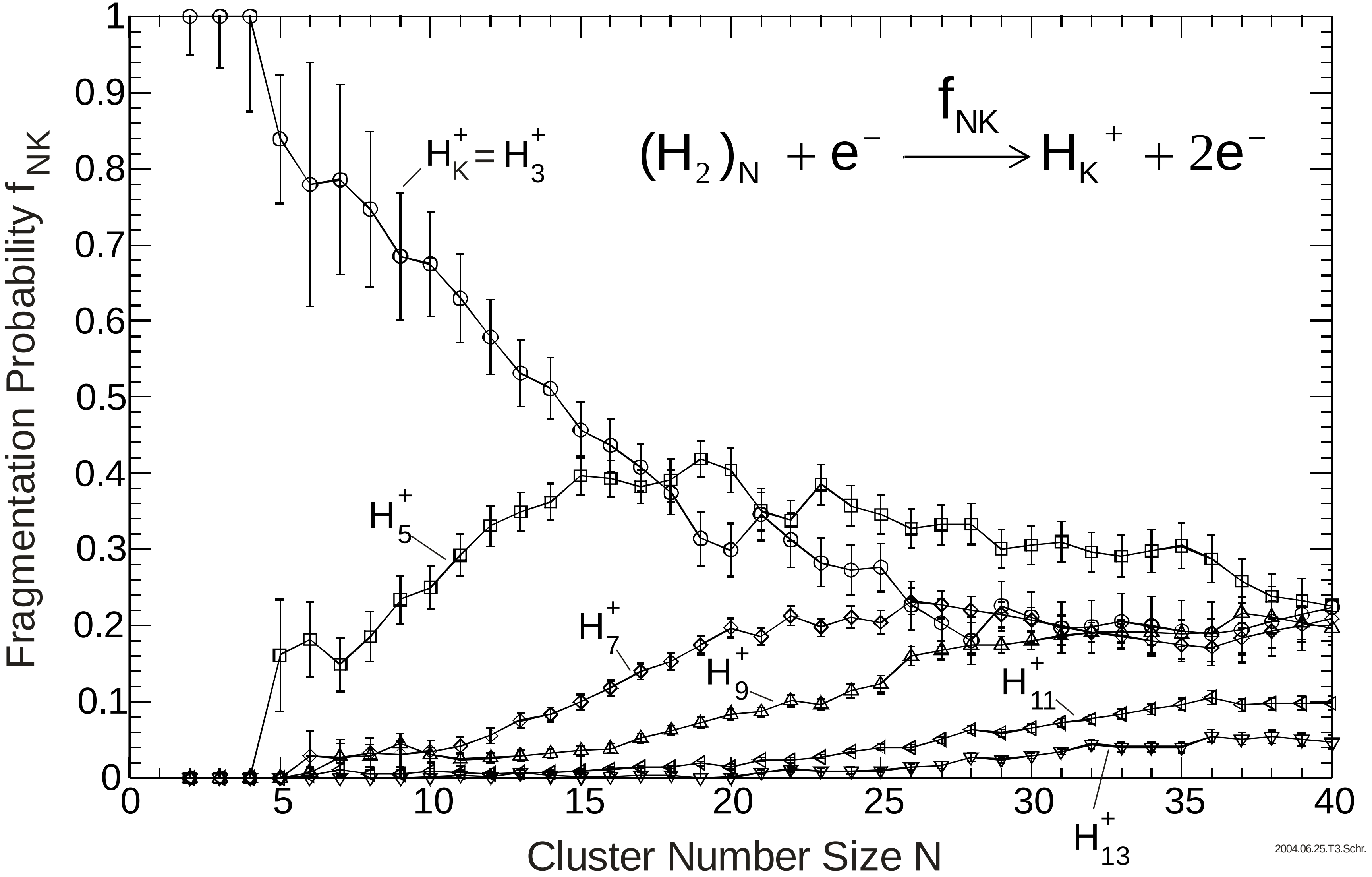




Kornilov and Toennies,
J. Chem.Phys.128,194306 (2008)

f_{NK}

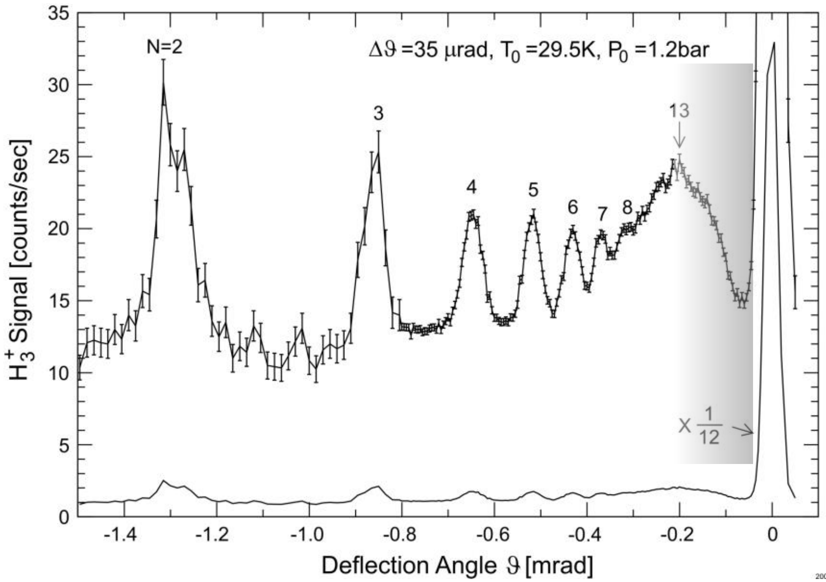
Fragmentation Probabilities as a Function of Cluster Size N



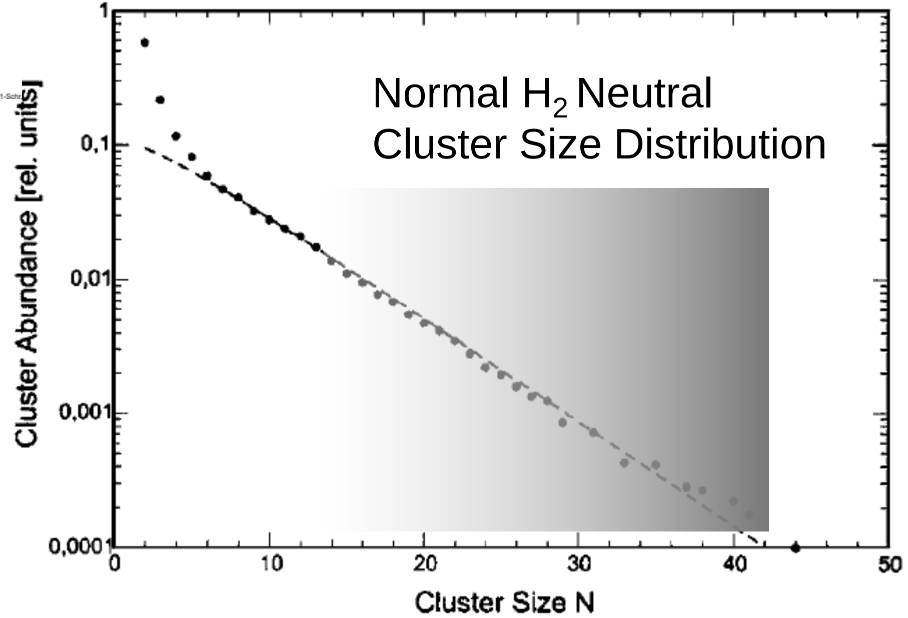
O. Kornilov and J. P. Toennies, in preparation

Size distr.

Determination of Neutral Cluster Size Distributions



$$G(N)=\frac{I_m(\theta)}{f_{NK}\cdot\sigma_{ion}}\left|\frac{\theta}{N^2}\right|$$



Normal H_2 Neutral Cluster Size Distribution

No Magic Numbers Seen with normal H_2!!

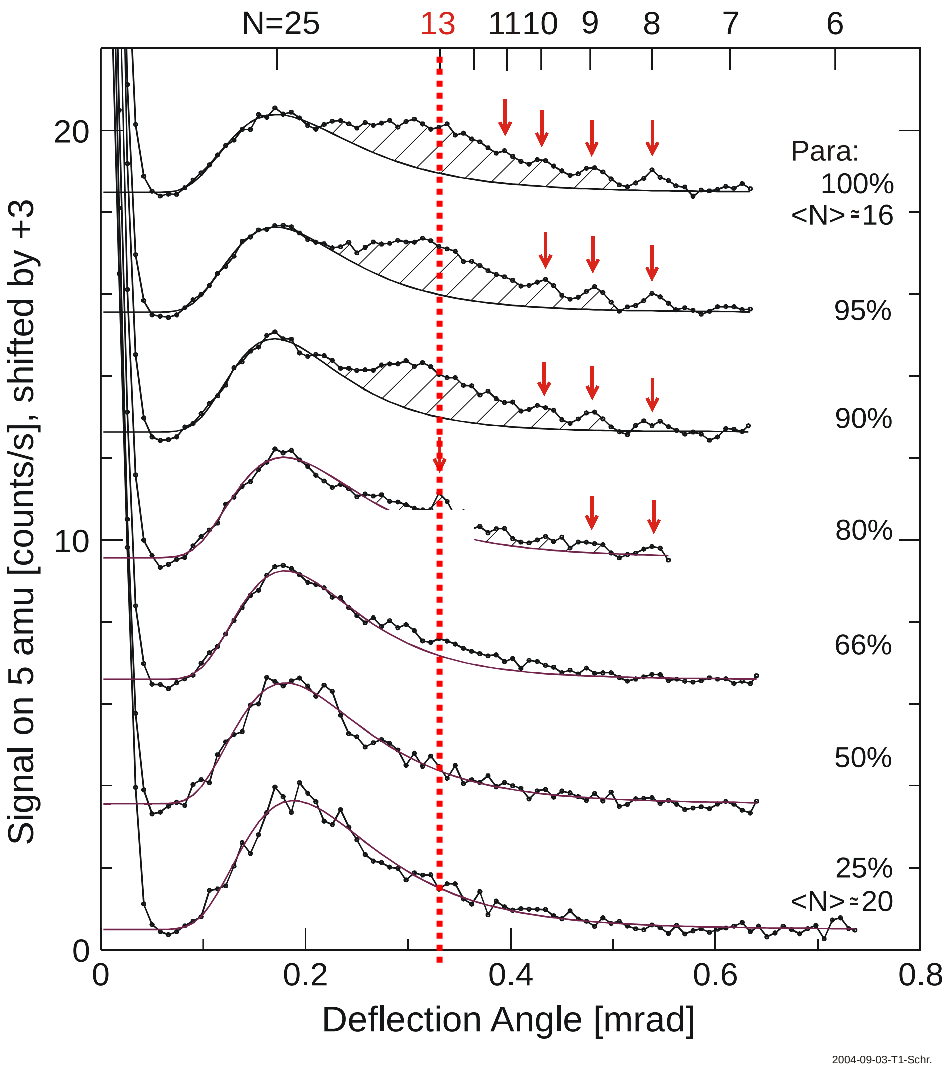
Magic no. with pH2

Kornilov and Toennies, J. Chem.Phys.128,194306 (2008)

Only para-H_2 Exhibits Magic Number 13

5% H_2 in He,
T_0=20K, P_0=3.5 bar

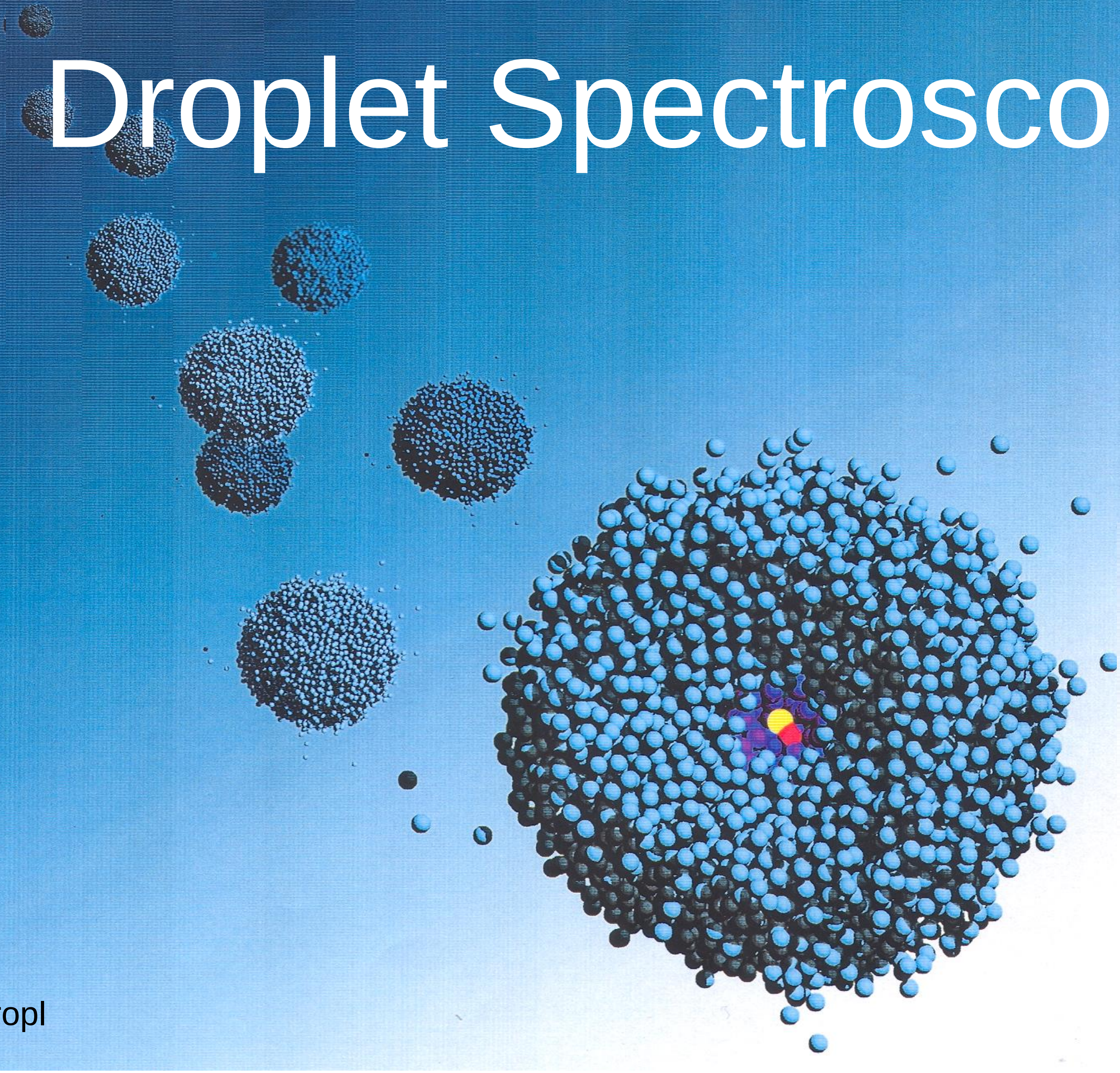
$T_{int} \leq 1.5$ K



Recent Calculations Indicate that Superfluidity is Suppressed by 3 or more Ortho-H_2 Molecules

Theory

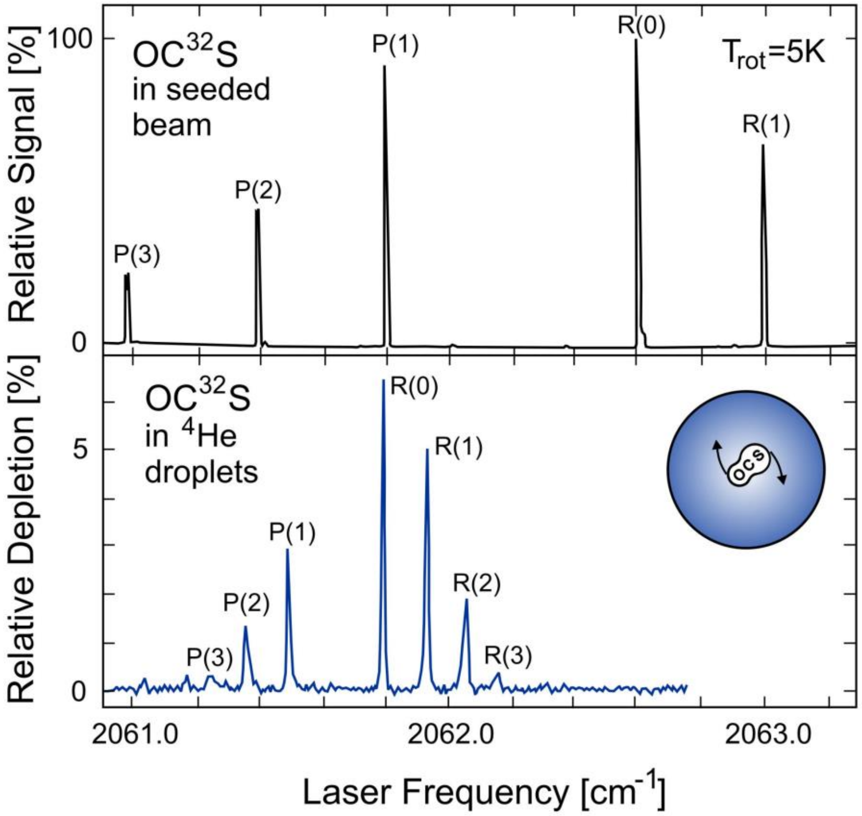
Droplet Spectroscopy



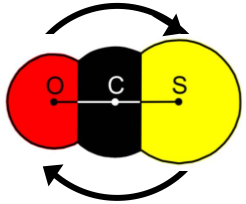
Rot in dropl

The Infra-red Spectra of Chromophore Molecules Inside Helium Droplets Indicate that the Molecules Rotate Freely.

A Microscopic Manifestation of Superfluidity



Boltzmann Plot of Intensities yields T_{Drop}=0.37K



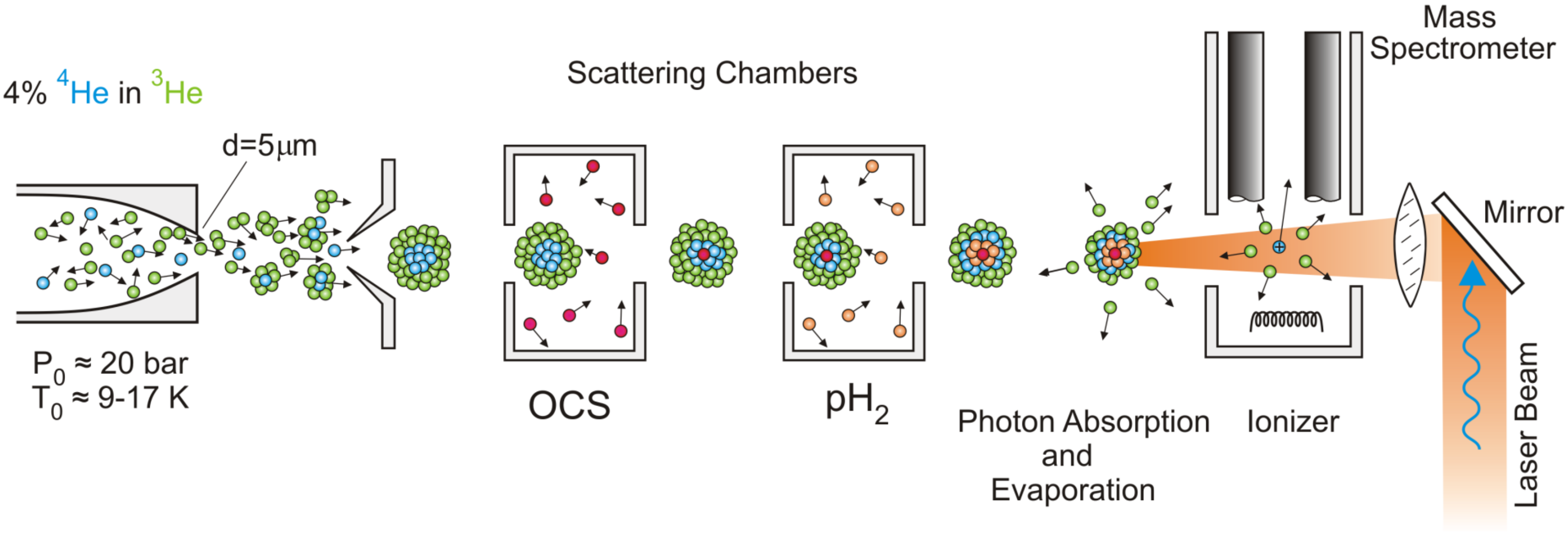
Sharp spectral features indicate that the molecule rotates without friction

The closer spacing of the lines indicates a factor 2.7 larger moment of inertia

app

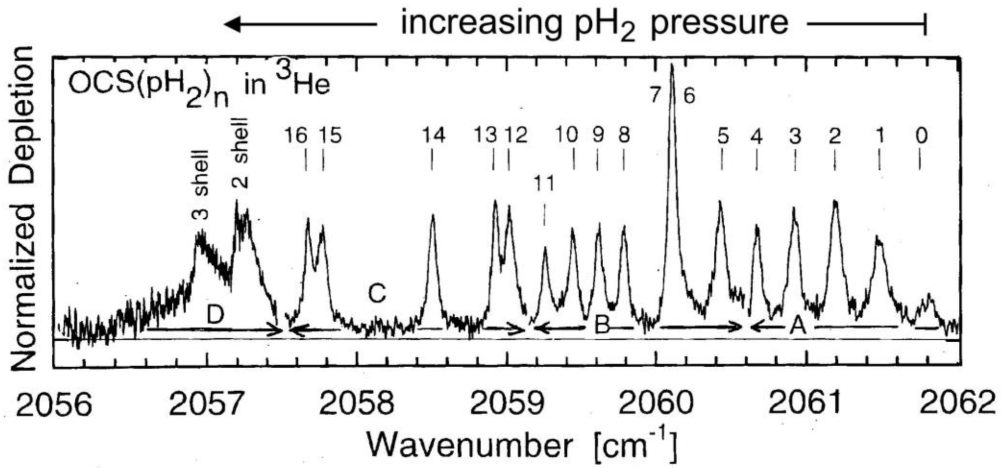
a) R. W. McKellar, private communication
b) S. Grebenev et al. Science 279, 2083(1998); J. Chem. Phys. 112, 4485(2000)

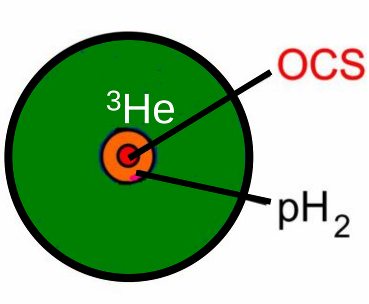
OCS-$(pH_2)_N$ Clusters are Assembled Inside ^{4}He Droplets or Inside Mixed ^{4}He/^{3}He Droplets

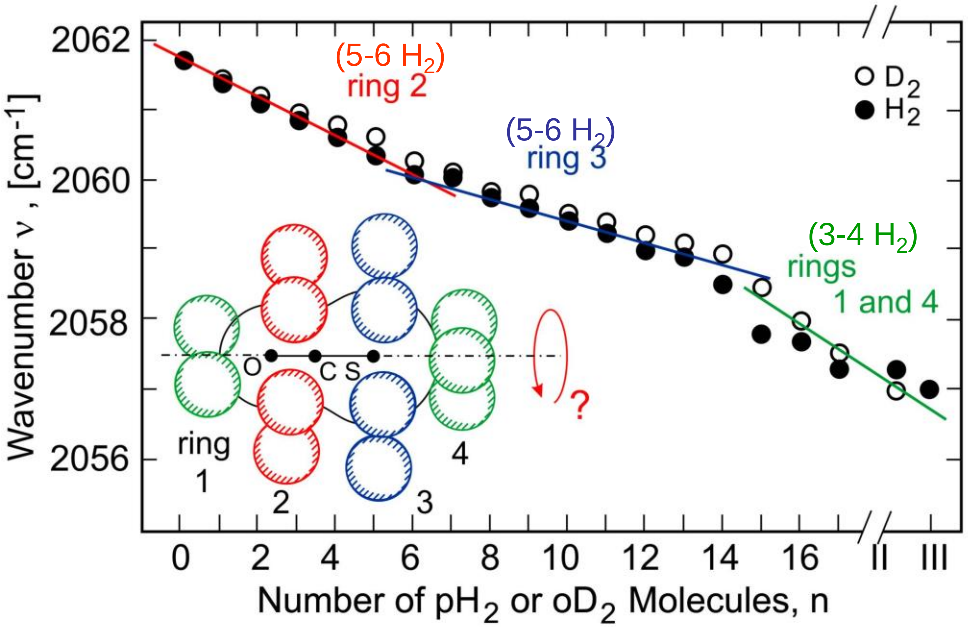


3He spect

The Line Shifts of Resolved Cluster Peaks in Pure ^{3}He Droplets Indicate Ring Growth



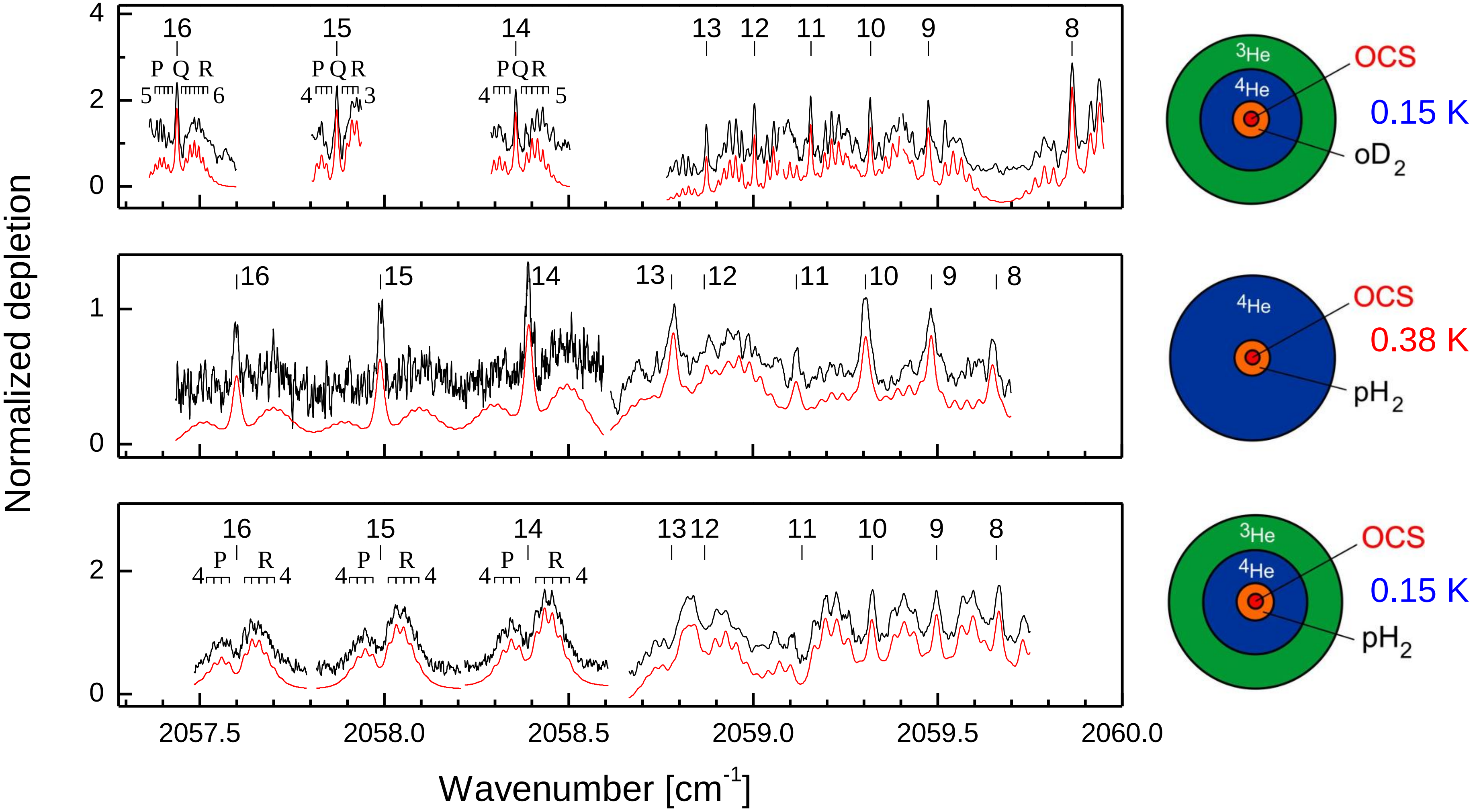




Q-branch

Grebenev, Sartakov, Toennies, and Vilesov, Science 289, 1532 (2000)

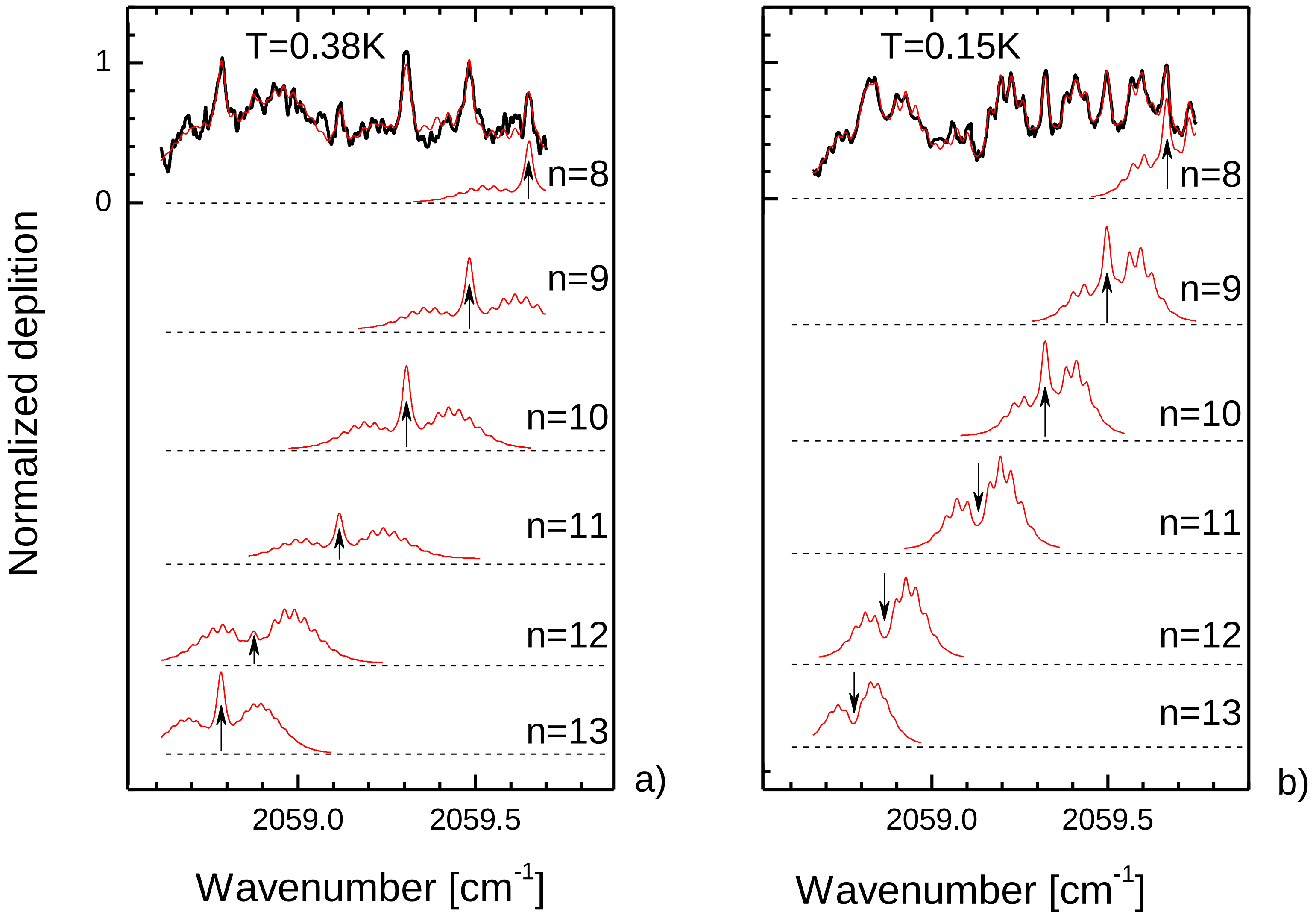
On Cooling from 0.38 to 0.15 K the Q-Branch remains for the o-D_2 Clusters but Vanishes for the p-H_2 Clusters



The Q-branch indicates that the cluster rotates about its symmetry axis

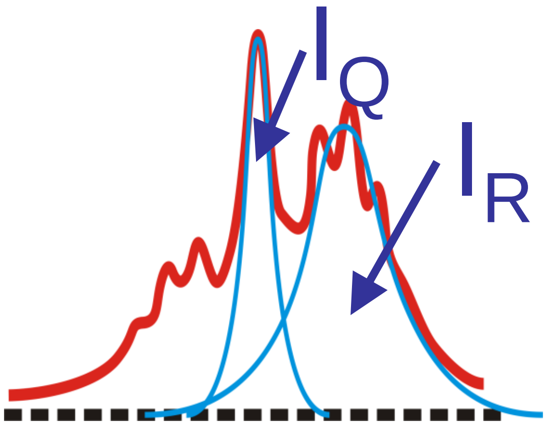
Grebenev, Sartakov, Toennies, and Vilesov, European Physics Lett. In print

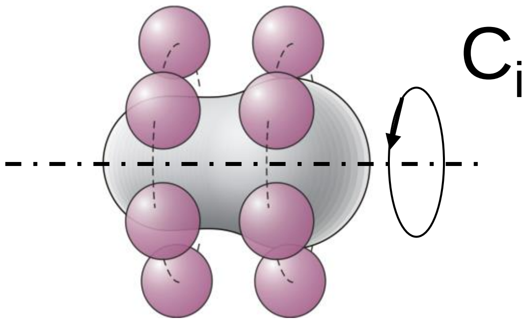
The Deconvolution of the Spectra Reveals that the Anomaly Starts at n ≥ 11 (except n = 12)



Grebenev, Sartakov, Toennies, and Vilesov, European Physics Lett. In print

The Spectrum is Characterized by the relative Areas of the Q- and R-Branches





$$I_Q \propto \sum_{JK} F(K,J)\, g_{JK}\, w_{JK}\, \exp\left[-E_{rot}(J,K)/kT\right]$$

$$I_R \propto \sum_{JK} G(K,J)\, g_{JK}\, w_{JK}\, \exp\left[-E_{rot}(J,K)/kT\right]$$

where for distinquishable particles $w_{JK} = 1$

indistinquishable particles $w_{JK} = \delta_{k,m\cdot i} \quad m = 0,1,2\ldots$

The experimental ratio I_Q/I_R depends on the axial symmetry of the cluster C_i

Drop in I_Q/I_R at T = 0.15 K for N ≥ 11 (except. 12) Corresponds to Large Increase in Symmetry *i*

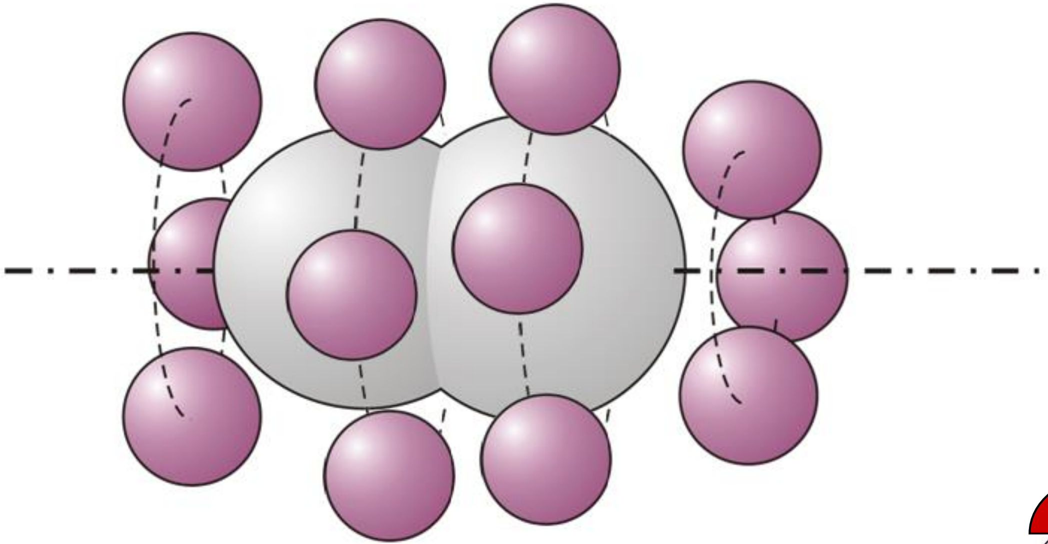
N	**T = 0.38 K**	***i***	**T = 0.15 K**	***i***	
10	0.56 ± 0.05	≤ 2	0.48 ± 0.04	1	same
11	0.51 ± 0.17	≤ 3	≤ 0.09	≥ 5	increase
12	≤ 0.19	≥ 6	≤ 0.07	≥ 4	same
13	0.62 ± 0.24	≤ 3	≤ 0.07	≥ 4	increase
14	0.69 ± 0.15	≤ 2	≤ 0.07	≥ 4	increase
15	0.64 ± 0.20	≤ 3	≤ 0.07	≥ 5	increase
16	0.62 ± 0.20	≤ 3	≤ 0.07	≥ 5	increase

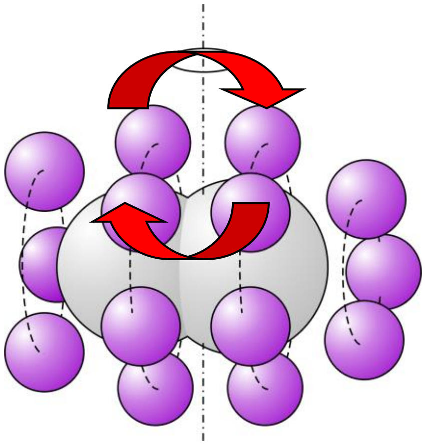
Grebenev, Sartakov, Toennies, and Vilesov, European Physics Lett. In print

animation

From the Ethane Molecule it is known that Hindered Rotations Double the Axial Symmetry

Wait 2 sec!

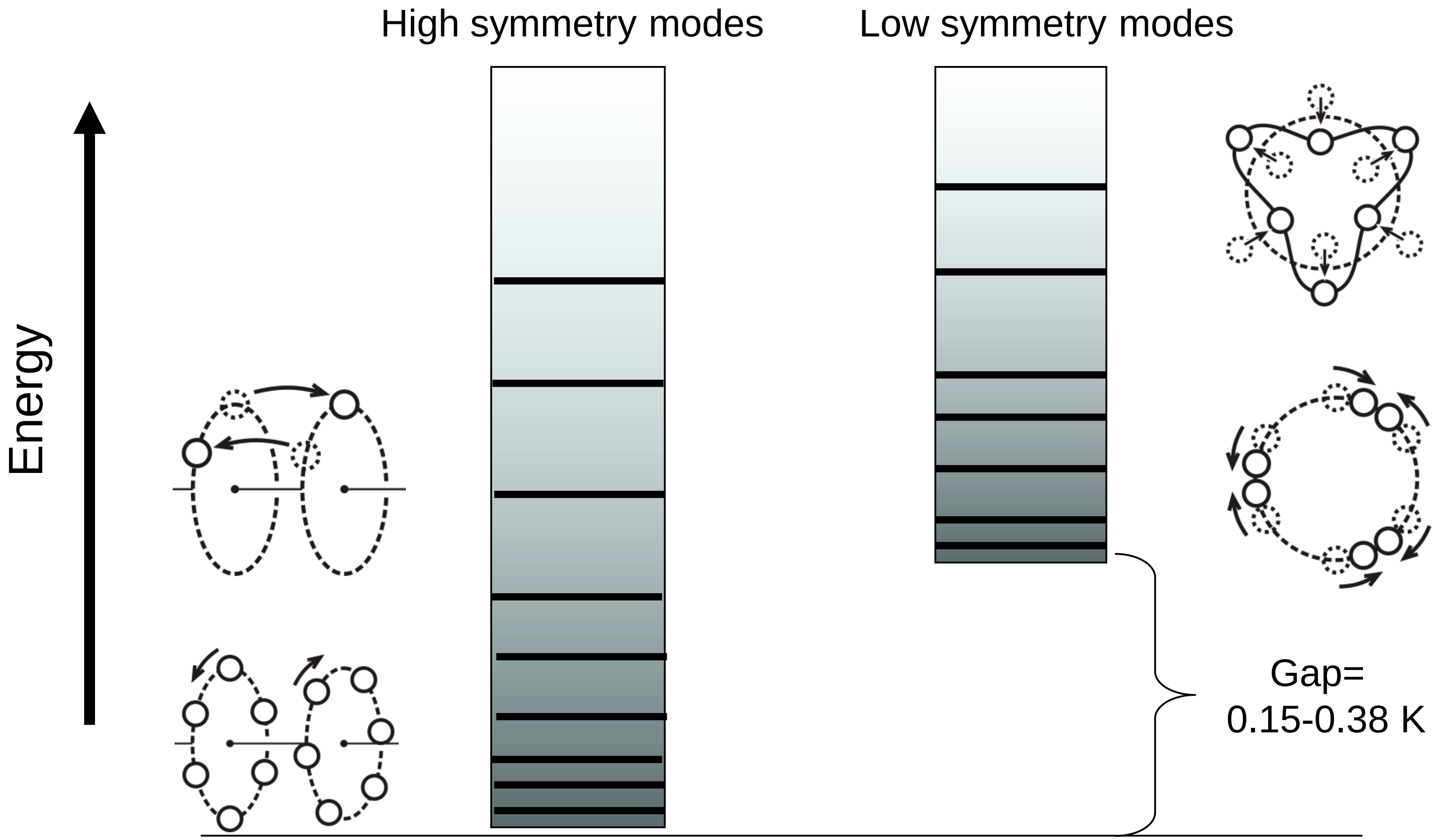




Here $C_6 \rightarrow C_{12}$

Energy levels

Postulated Energy Level Diagram



High symmetry modes

Low symmetry modes

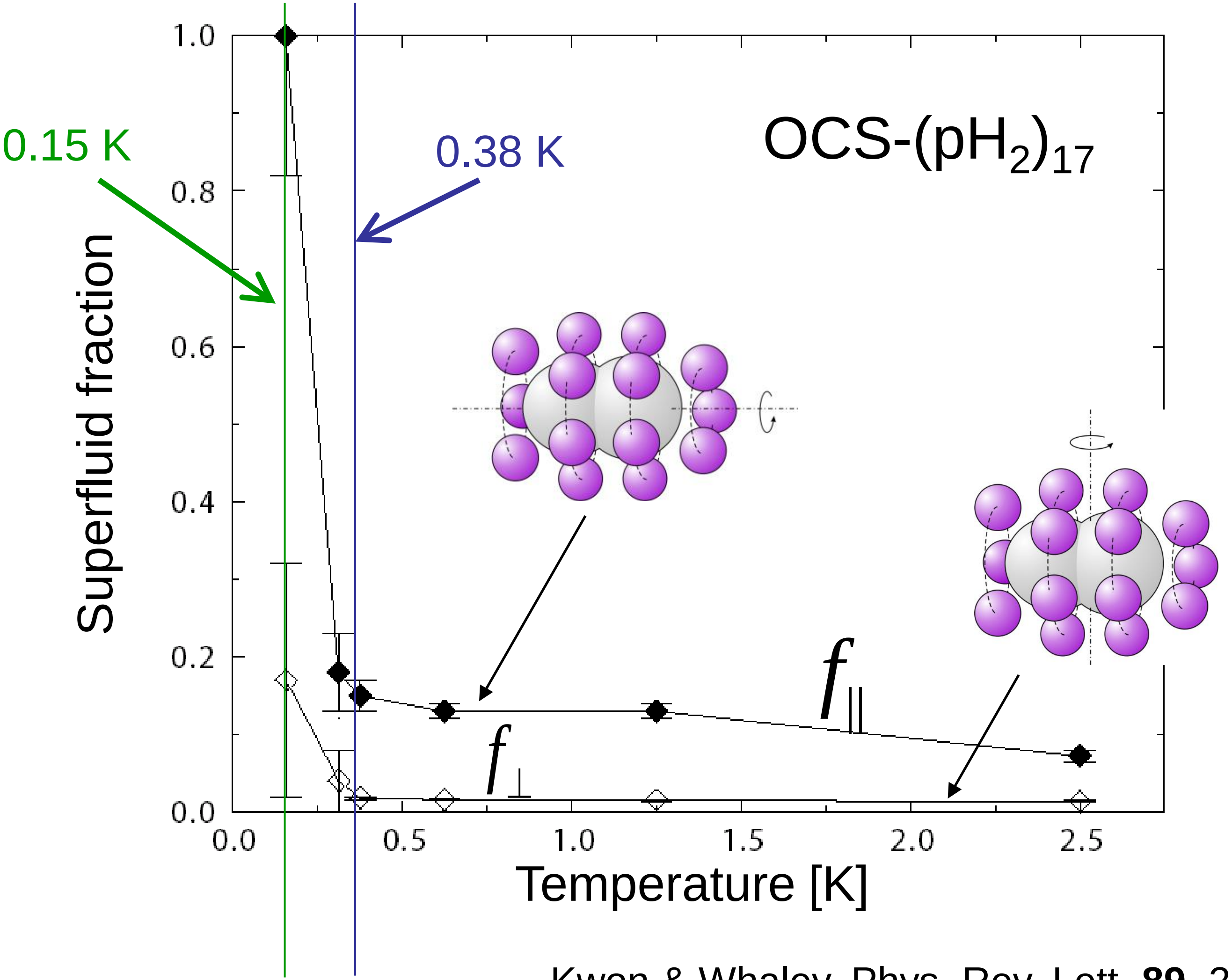
Energy

Gap=
0.15-0.38 K

Is this Really Superfluidity??

Kwon and Whalley

Yes, We Think So Since the PIMC Calculations also Predict a Superfluid Axial Response at About the Same Temperature



concl

Kwon & Whaley, Phys. Rev. Lett. **89**, 273401 (2002)

Summary

Small H_2 Clusters ($N \leq 26$) are fascinating objects exhibiting superfluidity while at the same appearing to be solid

The few experiments confirm the existence of magic numbers in pure para H_2 clusters, but not in normal H_2 clusters. Do magic nos. correlate with superfluidity??

Only evidence for superfluidity comes from experiments with doped clusters.There the effect is attributed to low frequency modes of high axial symmetry which facilitate particle exchanges

poem

HYDROGEN I

This molecule hydrogen is so very small
Yet it is the most abundant of all

It only has atoms two,
And as many electrons too.

It‘s every theoreticians delight,
they think they can calculate it just right.

President George Bush says its great stuff
to fight global warming it is enough!

Even though Ginzburg had a theory convincing.
It‘s superfluidity is no simple thing!

HYDROGEN II

It seems not so difficult after all,
if clusters like the molecule are small

Doping with OCS provides a clue
But still there is much for us to do!

Thank You!

Please Ask Questions!

End

Please Ask Questions!