Flying Cryostats: Superfluid Solvation and Molecular Motions in Helium Droplets

K. B. Whaley
UC Berkeley

Helium droplets are older than one might guess....

"Experiments on the condensation of helium by expansion"
H. Kammerlingh Onnes. Communication Nr. 105 of the
Physical Laboratory at Leiden (April 24, 1908)

... I had observed in expanding helium, which at a temperature of -259 °C had been strongly compressed...

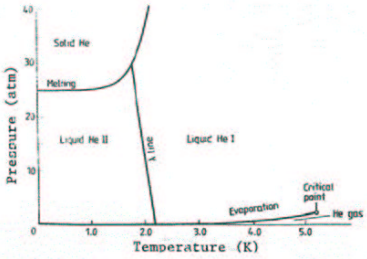
At the expansion of the helium a dense gray cloud appeared, from which separated solid masses floating in gaseous helium resembling cotton wool ...

... it is possible that the mist has been a liquid (helium) cloud

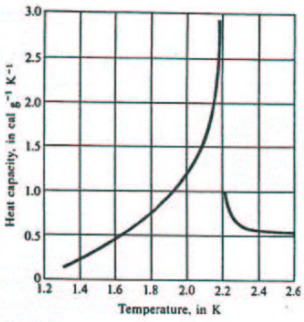
macroscopic sample of liquid helium achieved July 10, 1908
Nobel prize awarded for liquefaction in 1913

superfluidity of ^{4}He discovered in 1938 (Allen, Misener, Kapitza)

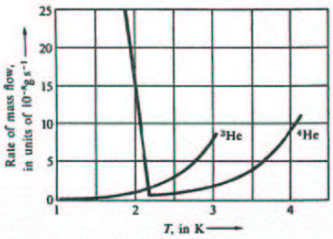
Superfluidity in bulk ^{4}He



phase diagram

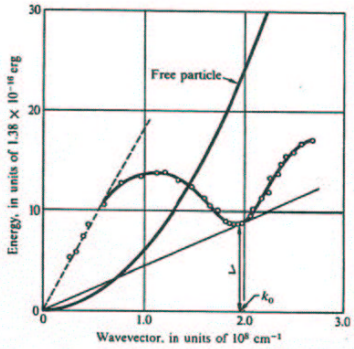


heat capacity



comparison of rates of flow under gravity through a fine hole

elementary excitations



Helium is 'self-cleaning': molecules aggregate, go to boundaries

REVIEW B VOLUME 29, NUMBER 7 1 APRIL 1984

Ultimate fate of a gas of atomic hydrogen in a liquid-helium chamber: Recombination and burial

Isaac F. Silvera
Lyman Laboratory of Physics, Harvard University, Cambridge, Massachusetts 02138
(Received 30 September 1983; revised manuscript received 12 October 1983)

In this article we consider the evolution in time of a gas of atomic hydrogen. Gaseous atomic hydrogen is produced in a cell in which the walls are coated with a film of liquid helium to reduce surface recombination. "Stabilized" spin-polarized hydrogen is at best long lived, slowly decaying away by recombination to the molecular state. We describe an experiment which leads to the conclusion that the resultant H_2, either in the form of single molecules or molecular clusters, penetrates the surface of the liquid helium and finally attaches to an underlying wall. The experimental technique developed for this study introduces a new method for producing atomic or molecular clusters at low temperature, either in a helium "background" gas or in liquid helium.

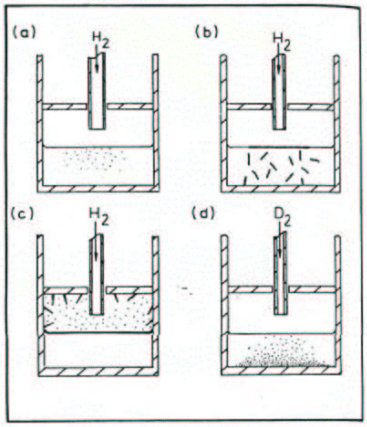
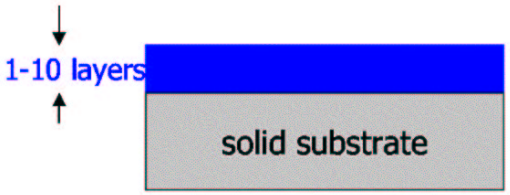
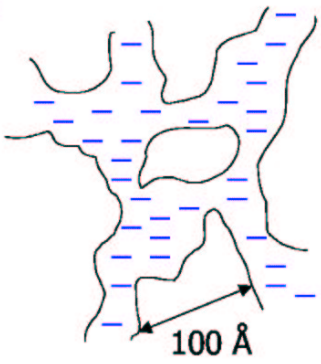


FIG. 5. Results of visual observations: (a), (b), and (c) H_2 flowing into liquid helium under low-, medium-, and high-flow conditions, respectively; (d) D_2 flowing into liquid helium.

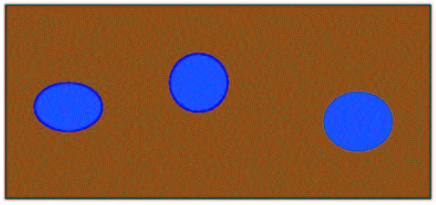
Superfluidity in confined geometries:



He films

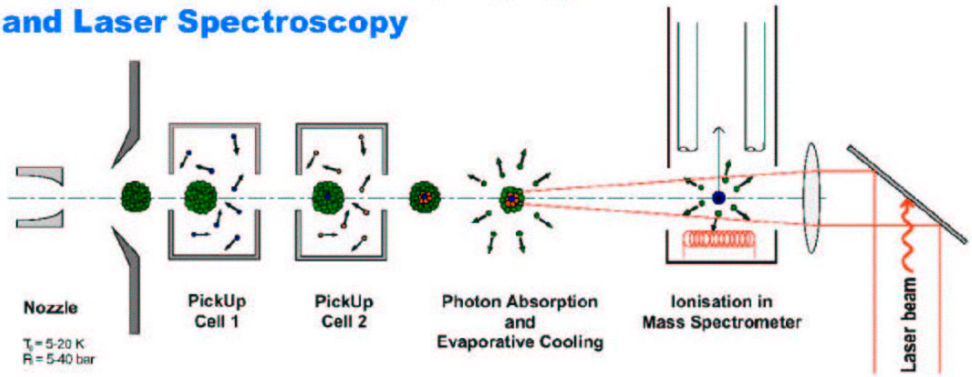


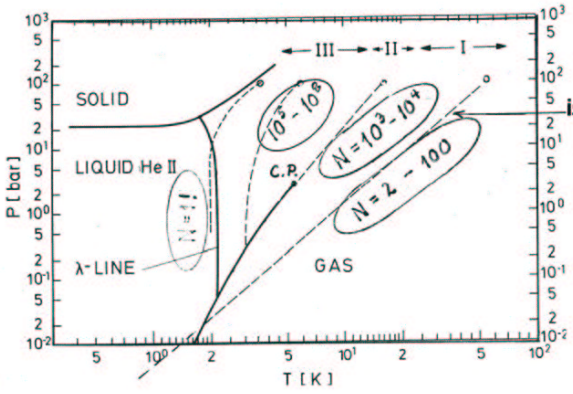
He in aerogel



He bubbles in Cu matrix under pressure

Helium Droplet Formation, Doping, and Laser Spectroscopy



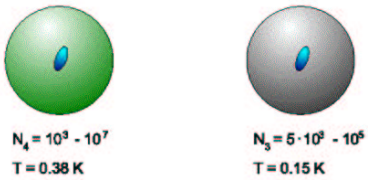


size of cluster, N, controlled by nozzle conditions

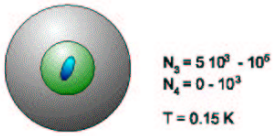
J. P. Toennies, et al. (Goettingen)

The Droplet Zoo

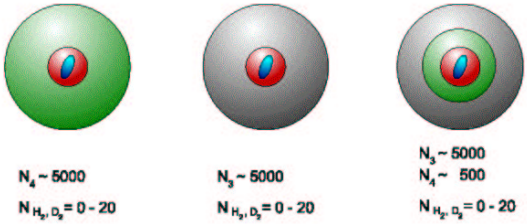
1. **Pure ^{4}He and ^{3}He Droplets**



2. **Mixed ^{4}He/^{3}He Droplets**



3. **Doping by p-H_2 (>99%), o-D_2 (~96%)**



A. Vilesov

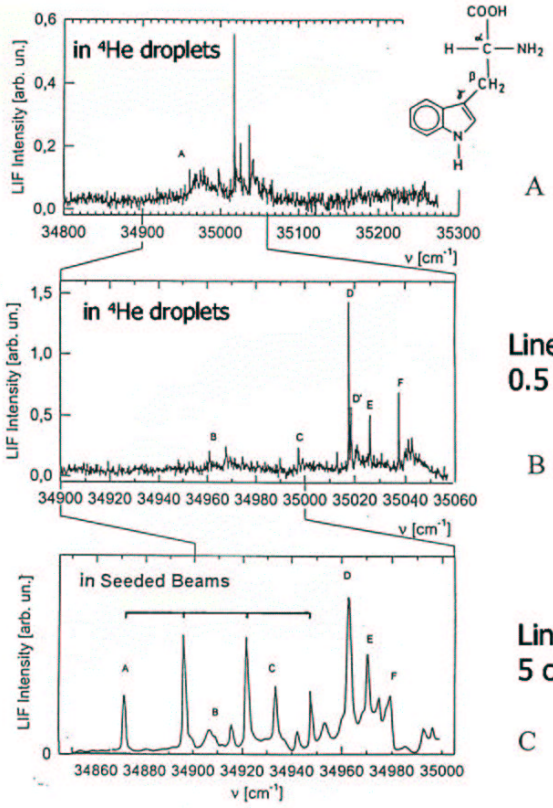
He Droplets

- Cold environment: T=0.37 K (0.15 K) and superfluid (^{4}He)
- Gentle quantum matrix for spectroscopy
- High resolution spectroscopy - probe of solvent effects in simple system (but quantum….)
- He droplets can be used to assemble molecular, metal, and other clusters, to pick up biological molecules, semiconductor nanocrystals, etc., for spectroscopic study…
- Chemical reactions, unstable species - low temperature control

for an overview see Toennies et al., Physics Today, Feb. 2001

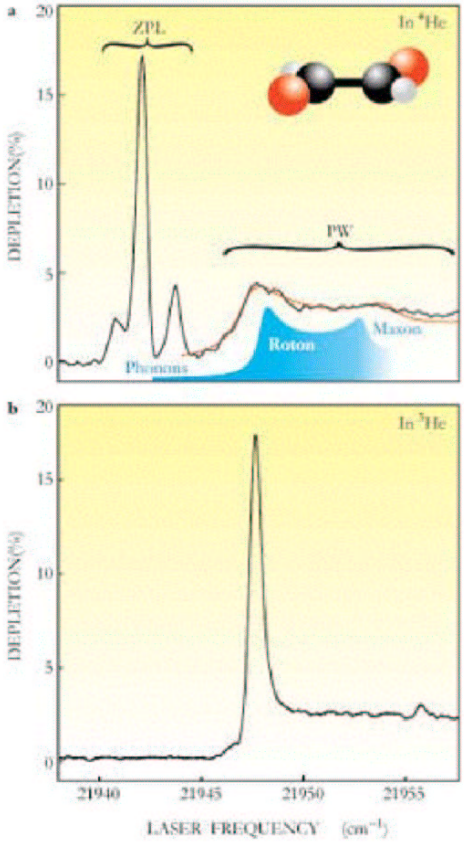
Sharp spectra:

LIF spectra of an amino acid tryptophan



Lindinger et al.
JCP 110, 1429 (1999)

Evidence of superfluidity in ^4He_N:

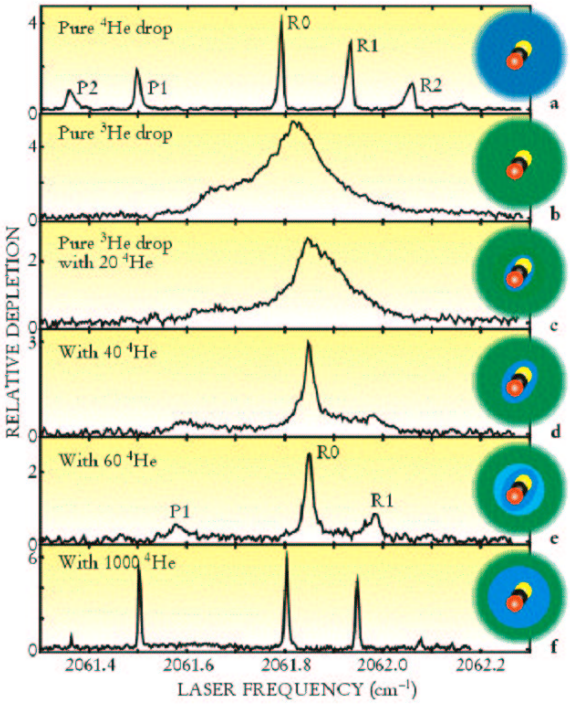


electronic excitation of gloxal molecule ($C_2H_2O_2$)

in ^4He_N - gap, phonon wing fit to ~ bulk DOS
in ^3He_N - no gap

S. Grebenev et al., Physica B 280, 65 (2000)

IR Spectrum of OCS in helium droplets



free rotation in ^{4}He

rotational diffusion in ^{3}He

linear molecule Hamiltonian
reduced spacing → $B < B_0$

Grebenev et al. (Science 1998)

Free rotation

Rotational diffusion

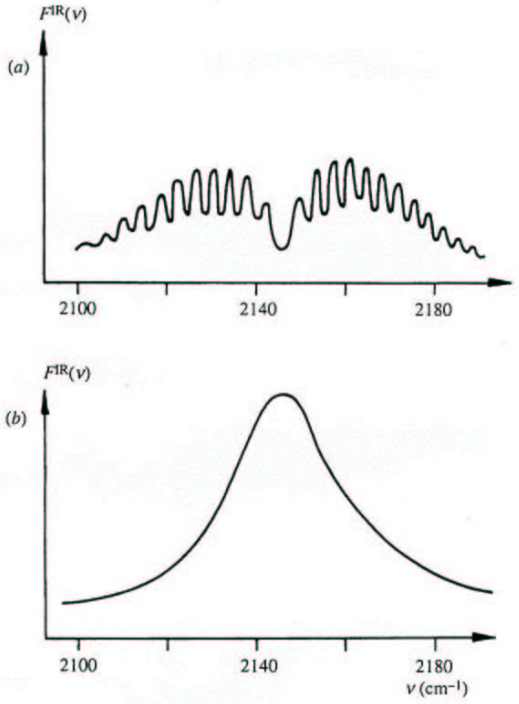
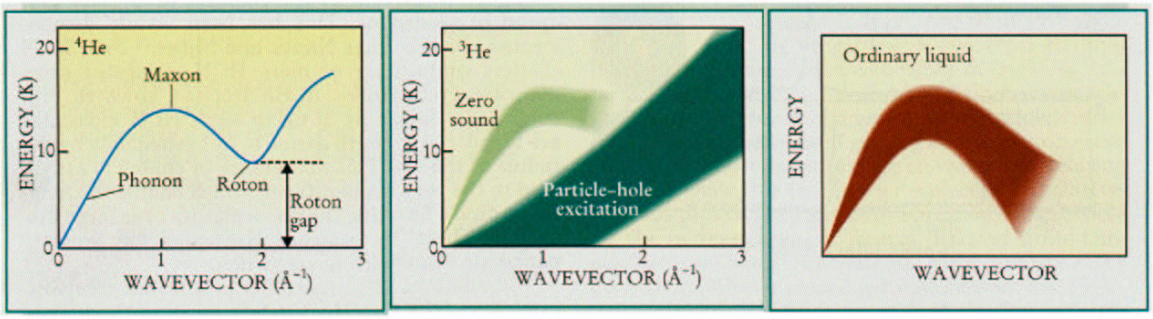


Fig. 0.1. Infrared absorption spectrum of CO in gas (*a*) and liquid (*b*) at 80 K

Spectra of elementary excitations



Babichenko and Kagan: PRL 83, 3458 (1999)
lower spectral density of states coupled to rotational levels of molecule in ^4He_N

Rotational constants in ^{4}He droplets T~0.38 K, N~1000

[B] = cm^{-1}

Molecule	B_0	B in ^4He_N	B/B_0 (%)	ref.
HF	19.78	19.48	98	1
NH3	9.94	7.5	76	2
HCN	1.478	1.175	79	3
HCCH	1.182	1.048	89	4
OCS	0.20	0.073	37	5
HCCCN	0.15	0.052	33	4
SF6	0.091	0.034	36	6
$(HCN)_2$	0.058	0.019	33	4

1) Nauta et al. (JCP 2000)
2) Behrens et al. (JCP 1998)
3) Conjusteau et al. (JCP 2000)
4) Callegari et al. (PRL 1999)
5) Grebenev et al. (JCP 2000)
6) Hartmann et al. (PRL 1995)

Theory:

- direct calculation of rotational energy levels
  - DMC, POITSE
- density analysis
  - adiabatic following
- molecular rotation and superfluidity
  - local two-fluid theory
  - role of hydrodynamics

Diffusion Monte Carlo:

$$\frac{\partial \Psi}{\partial t} = -D\nabla^2\Psi + V\psi \qquad \text{diffusion with source/sink } V$$

$$\Psi(t) = e^{-\hat{H}t}\Psi(0) \qquad \Psi(t\to\infty) \sim \Phi_0(t)$$

importance sampling: $\Psi \to f = \psi_T \Phi$

$$\frac{\partial f}{\partial t} = -D\nabla^2 f + E_L f + F_Q f, \qquad E_L = \psi_T^{-1}\hat{H}\psi_T$$

$$F_Q = \nabla \ln|\psi_T|^2$$

use ψ_T to impose nodal structures → excited states

ψ_T has boson symmetry of ^4He_N

POITSE: (Projection Operator Imaginary Time Spectral Evolution)

spectral information from time evolution

$$\int_0^\infty e^{-\omega t}\kappa(\omega)d\omega = C(t) = \langle A(t)A(0)\rangle \qquad t = it_r$$

evaluate with Monte Carlo over ψ_T

cf. absorption spectra from real time

$$\int \mu(0)\mu(t_r)e^{i\omega t_r}dt_r \sim \sigma(\omega)$$

$$\kappa(\omega) = \mathcal{L}^{-1}[C(t)] = \frac{1}{2\pi}\int C(\omega)e^{\omega t}dt$$ spectral function → excitations

inversion made with maximum entropy method

Blume et al. (PRE 1997)

Rotational energy levels of molecules in ^4He_N: direct calculations

1. Imaginary time spectral evolution (POITSE)

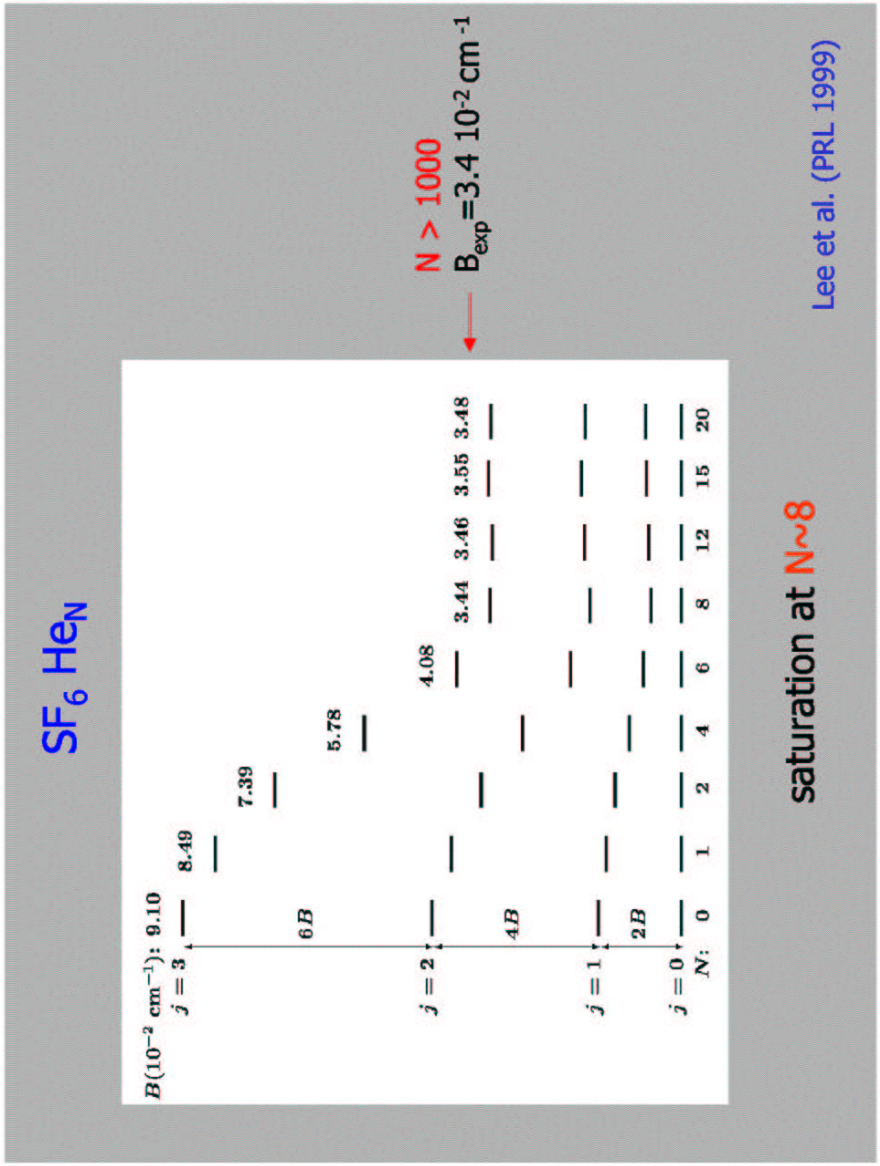
diatomics, SF_6	D. Blume	Blume et al. (JCP 1999)
HCN	A. Viel	Viel et al. (JCP 2001)
OCS	F. Paesani	

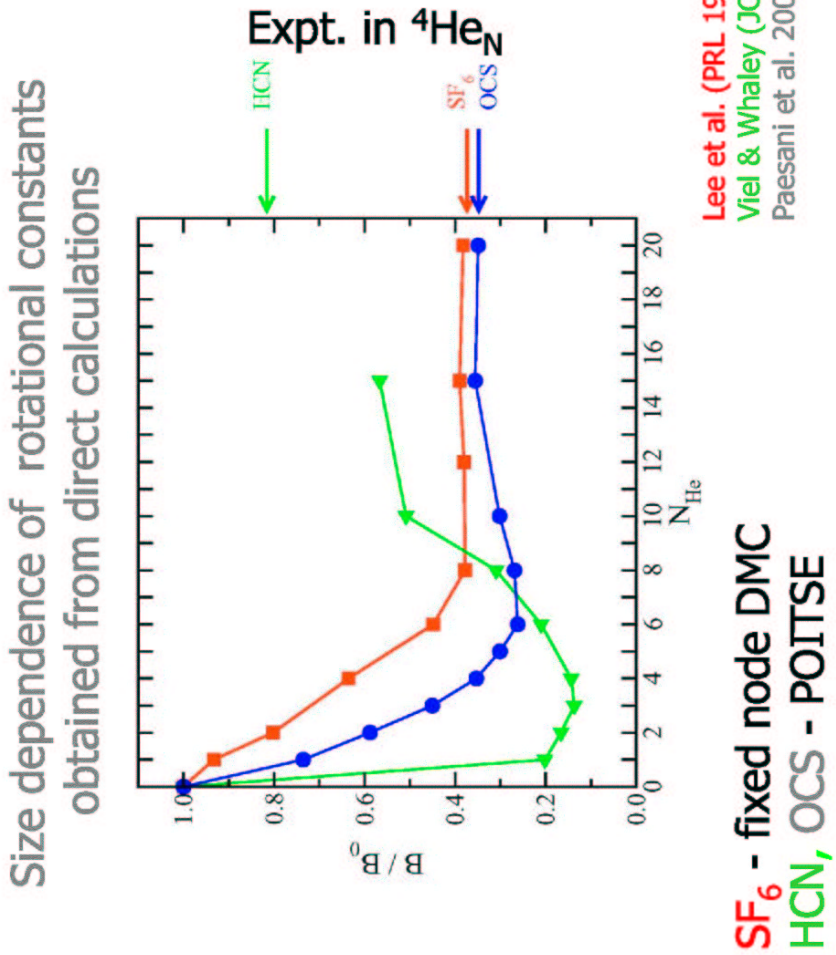
2. Fixed node DMC

– rotational importance sampling		P. Niyaz	Viel et al. (CPC 2002)
– fixed frame	SF_6	E. Lee	Lee et al. (PRL 1999)
– mixed frame	HCN	A. Viel	Viel et al. (JCP 2001)

3. Quasi-adiabatic approximation (Quack & Suhm'91)

OCS	F. Paesani	Paesani et al. (EPL 2001)


SF6 HeN
B(10^-2 cm^-1): 9.10
j = 3
8.49
7.39
6B
5.78
j = 2
4.08
4B
3.44
3.46
3.55
3.48
j = 1
2B
j = 0
N: 0 1 2 4 6 8 12 15 20
N > 1000
Bexp=3.4 10^-2 cm^-1
saturation at N~8
Lee et al. (PRL 1999)

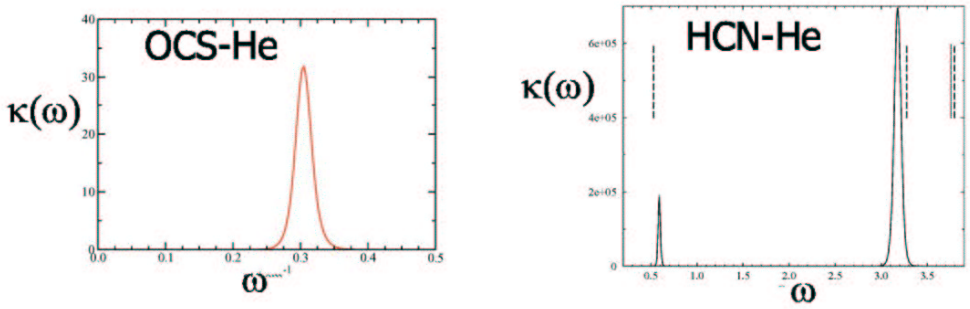

Size dependence of rotational constants
obtained from direct calculations
Expt. in 4HeN
HCN
SF6
OCS
B / B0
NHe
0.0
0.2
0.4
0.6
0.8
1.0
0 2 4 6 8 10 12 14 16 18 20
Lee et al. (PRL 1999)
Viel & Whaley (JCP 2001)
Paesani et al. 2002
SF6 - fixed node DMC
HCN, OCS - POTTSE

Nature of nodal surfaces for rotation:

Fixed node:

SF_6 - free molecule nodal surface ✓
HCN - free molecule nodal surface ✖

POITSE:



OCS - free rotation projector gives 1 peak
HCN - free rotation projector gives 2 peaks ⇒
more complex nodal surfaces

POITSE:

Spectral evolution (projector) Monte Carlo

$$\psi_e = \hat{A}\psi_0 \qquad J_0 = 0$$

$$\Delta J = j + l$$

compute spectral function

$$\kappa(\varepsilon) = \sum_f \left| \left\langle \psi_0 \middle| \hat{A} \middle| \psi_f \right\rangle \right|^2 \delta\left(E_f - E_0 + \varepsilon\right)$$

no nodal constraints

⟶ Extract excitations with $\Delta J \sim j$

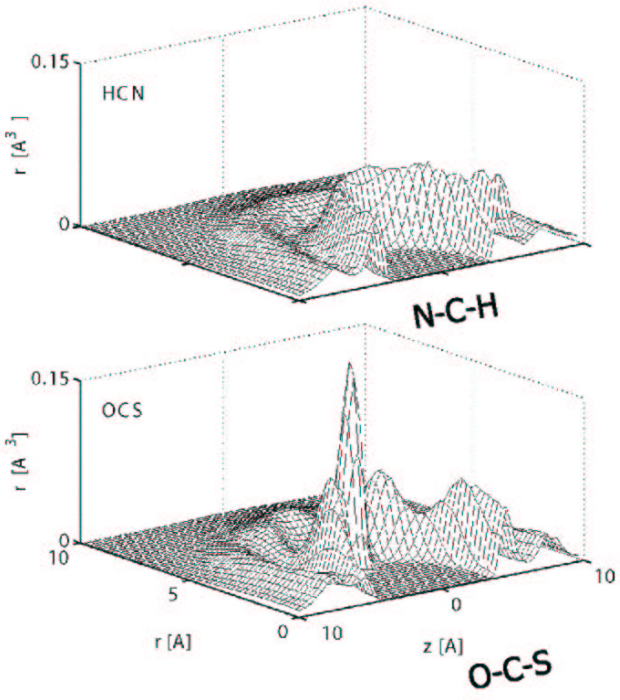
- no contribution to ΔJ from relative motion of He
- allows 'renormalization' of molecular motion via rigidly locked He rotation

DMC helium densities with/without molecular rotation

→ analysis of adiabatic following

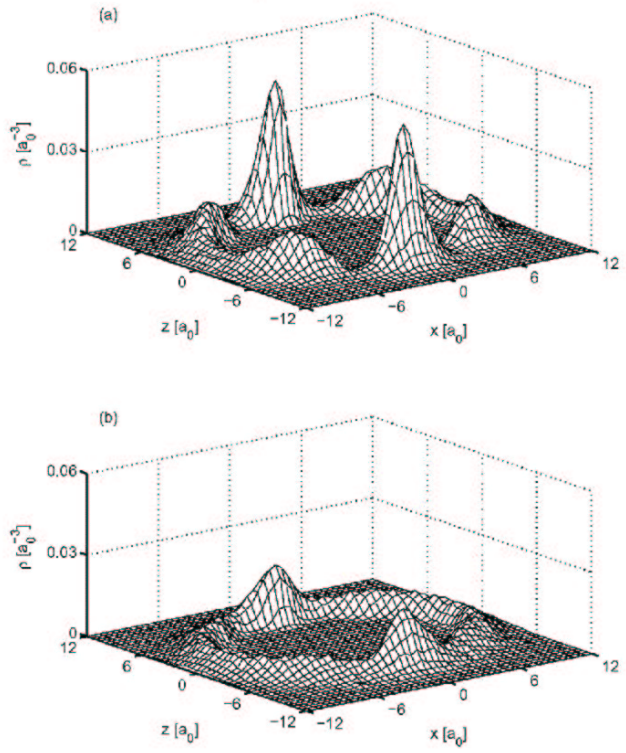
of molecular rotational motion by helium

Comparison of helium densities around HCN and OCS



N=64
PIMC
T=0.3 K

Helium density around benzene N=14

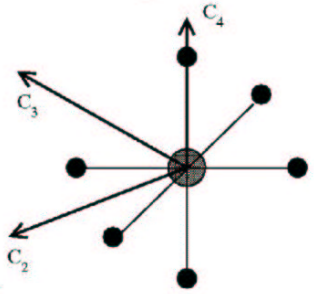


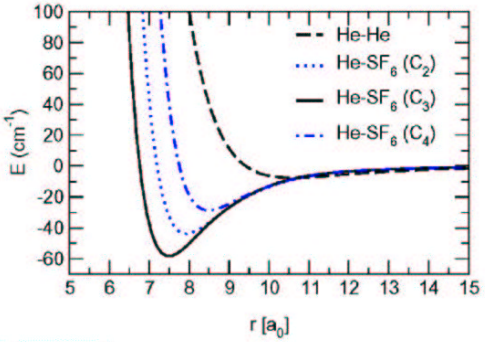
no benzene rotation

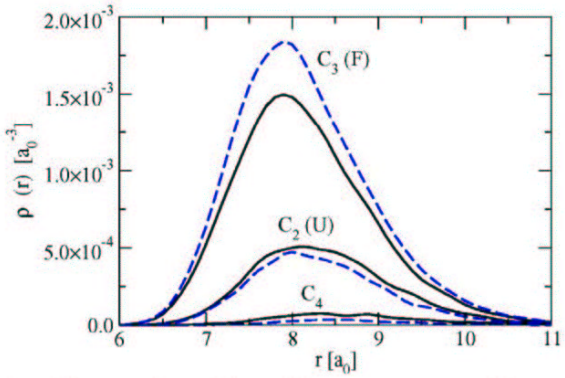
with benzene rotation

P. Huang

Quantification of Adiabatic Following: SF_6He_N



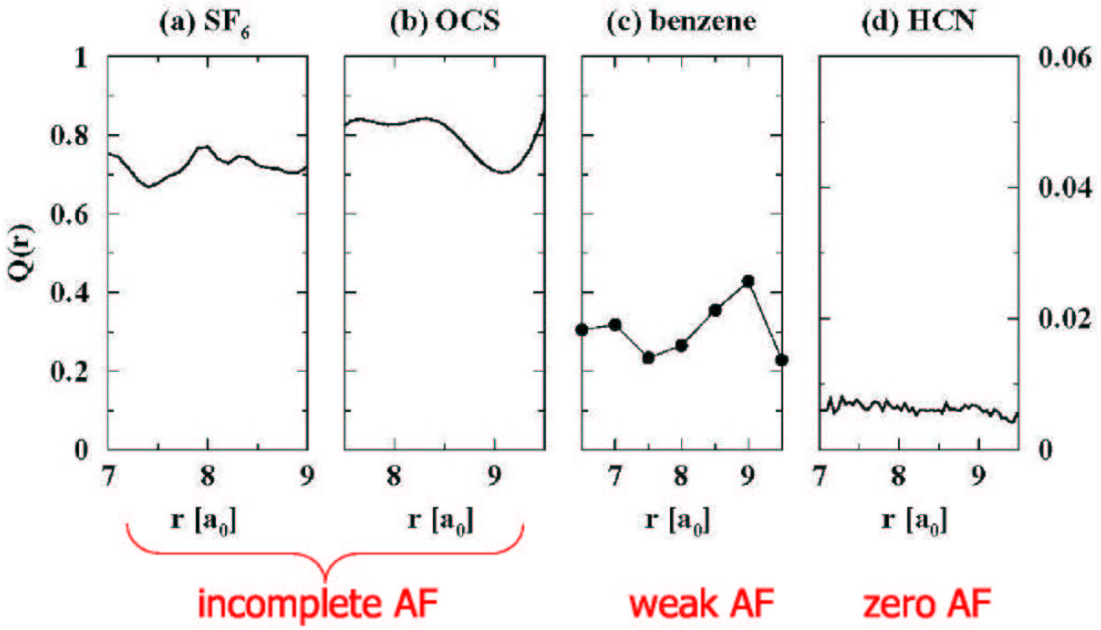




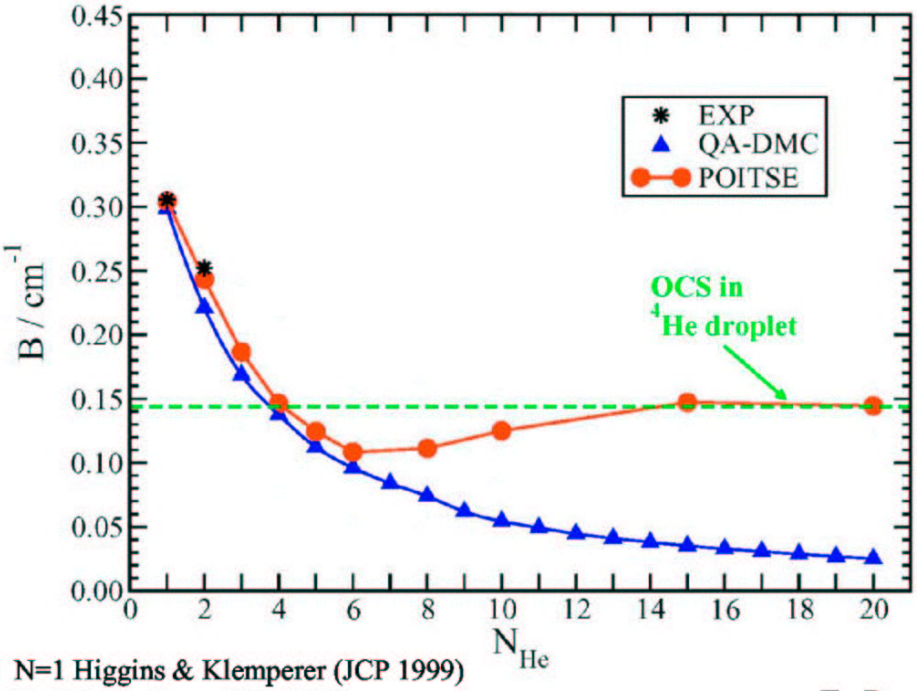
$$Q(r) = \frac{[\rho_U/\rho_F]_{norot}}{[\rho_U/\rho_F]_{rot}}$$

helium density along symmetry axes for n=1

Quantification of adiabatic following of Helium with molecular rotation: Q(r) for N=1 complexes

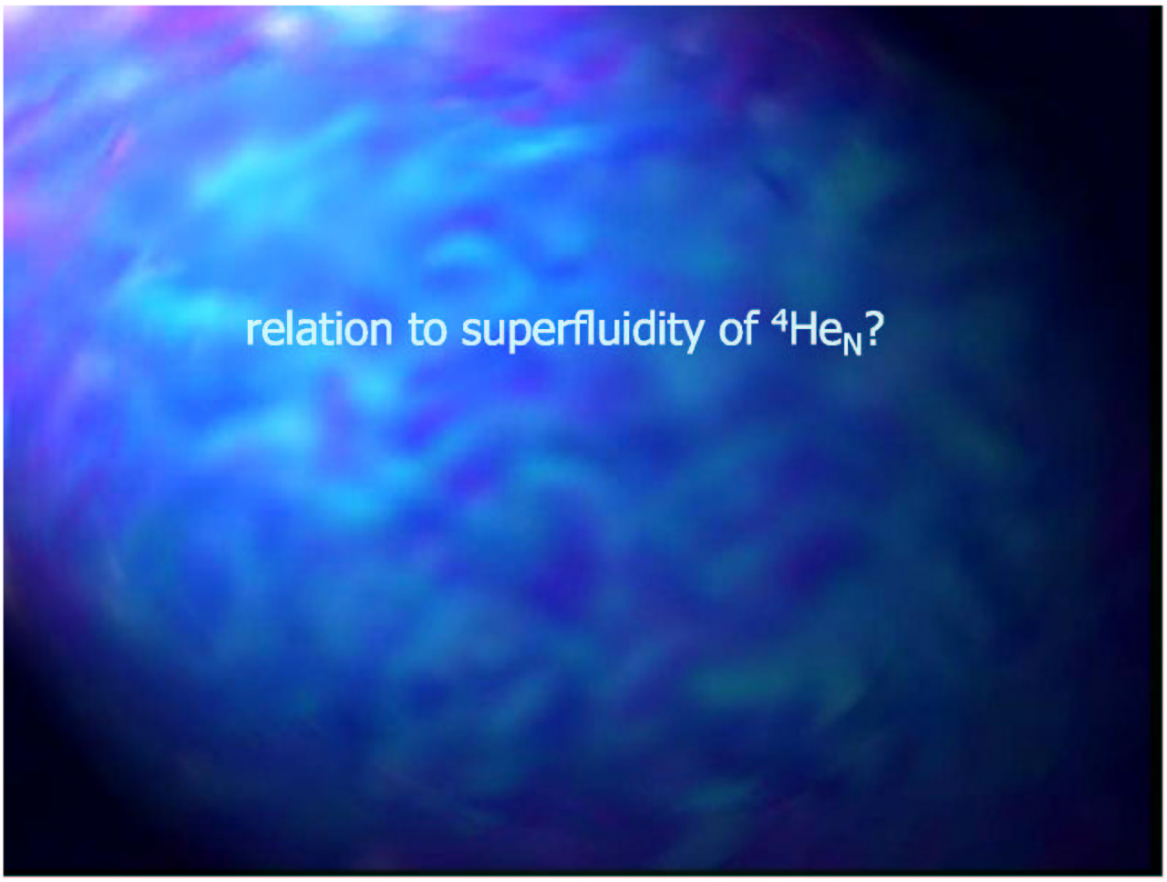


Rotational constant for OCS in ^4He_N - POITSE



* expt: N=1 Higgins & Klemperer (JCP 1999)
N=2 Xu & Jäger (CPL 2001)
----- N>1000 Grebenev et al. (JCP 2000)

F. Paesani



Kwon & Whaley (PRL 1999)
Kwon et al. (JCP 2000)

Microscopic two-fluid theory:

- local two-fluid decomposition of quantum solvation density
  - PIMC analysis
- molecule-induced non-superfluid density in first solvation shell
- two-fold helium response to molecular rotation
- adiabatic following of local non-superfluid $\rightarrow I_n$
  - rigid coupling
- adiabatic following of local superfluid $\rightarrow I_s$
  - possible hydrodynamic contribution

effective molecular moment of inertia $I = I_0 + I_n + I_s$

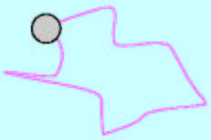
$\rightarrow$ rotational constant(s) B

Path integral Monte Carlo:

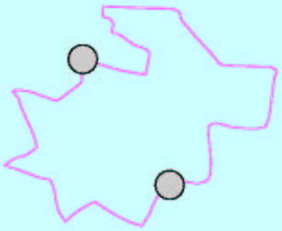
$$\langle O \rangle = Z^{-1} \int dR dR' \rho(R, R'; \beta) \langle R | \hat{O} | R' \rangle$$

$$\int \ldots \int dR_1 dR_2 \ldots dR_{M-1} \rho(R, R_1; \tau) \ldots \rho(R_{M-1}, R'; \tau)$$

$$\tau = \beta / M$$



Bose symmetry: $\rho(R, R'; \beta) = \frac{1}{N!} \sum_P \rho(R, PR'; \beta)$



generalized metropolis algorithm:

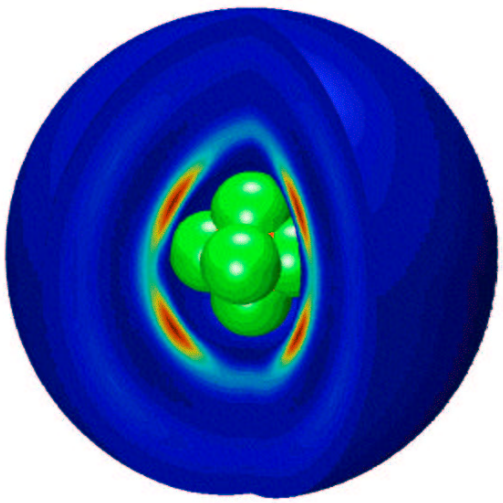
Ceperley and Pollock, PRB (1986)

$$\langle O \rangle \cong \sum_{\substack{paths \\ \alpha}} \langle R_\alpha | \hat{O} | R'_\alpha \rangle$$

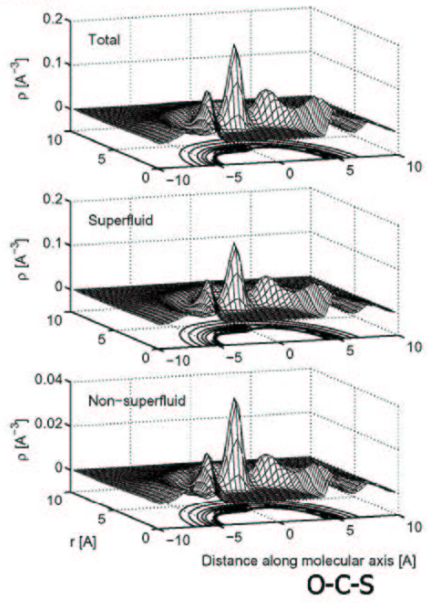
X^4He_N: input V, T, N

local two-fluid density decomposition: $\rho_{tot}(r) = \rho_s(r) + \rho_n(r)$

SF_6



OCS



$\rho_n(r)$ molecular-interaction induced non-superfluid density

I. Adiabatic Following of local non-superfluid:

$$KE(\rho_{ns}) < V_b$$

	$KE(\rho_{ns})$	V_b	$V_b(rigid\ rot.)$	He follows ?
SF_6	0.42	21	43	✔
OCS	1.15	42	118	✔
HCN	29	14	25	✘

(energies in K)