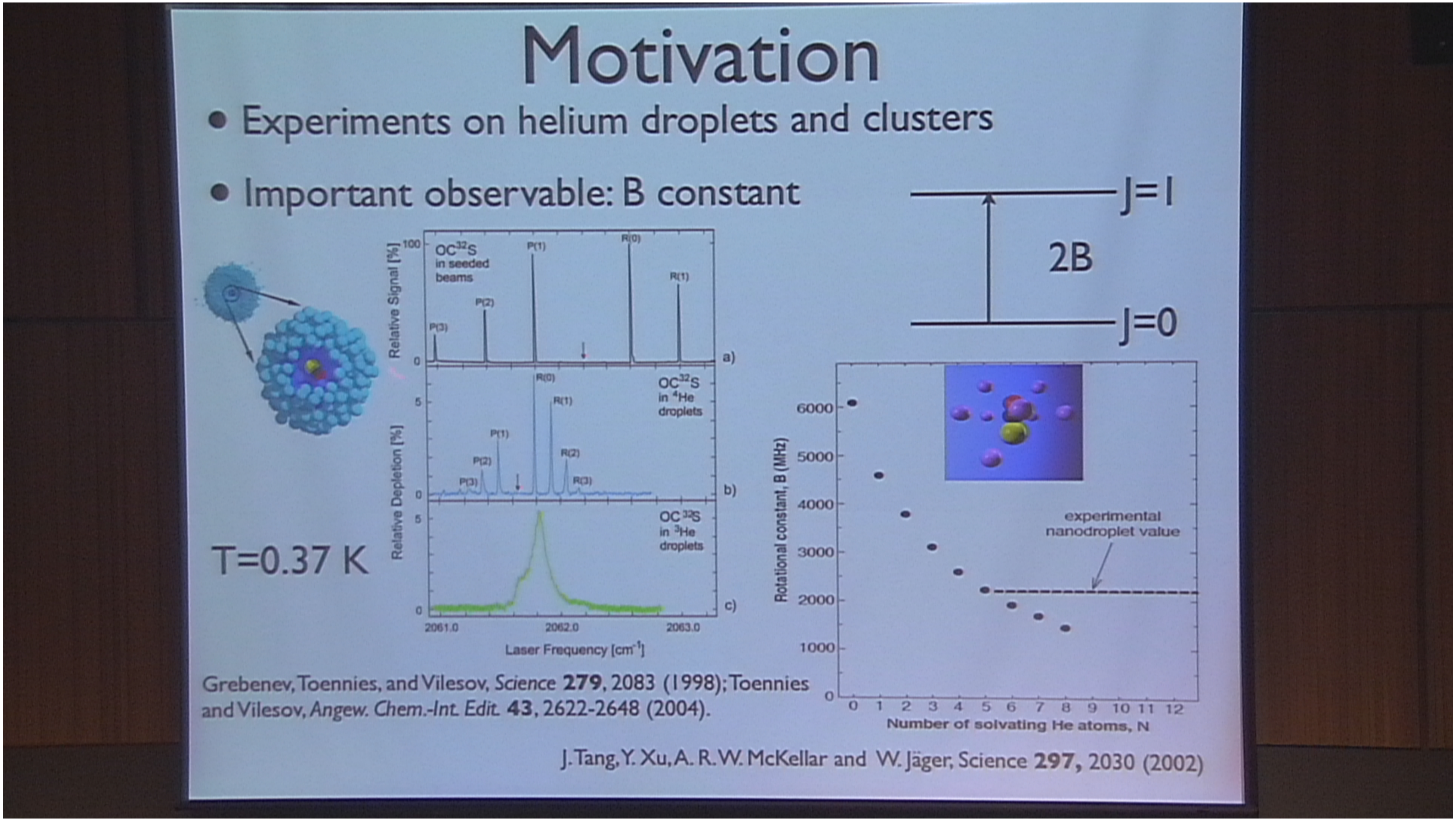
Title: Molecular rotation in doped superfluid clusters

Date: May 03, 2012 02:30 PM

URL: http://pirsa.org/12050038

Abstract: Experiments where impurities were incorporated into helium nanodroplets have shown that the impurity freely rotates, and this has been attributed to the superfluidity of the nanodroplet [1]. Results from experiments with smaller helium clusters suggest that the onset of superfluidity is linked to system size and bosonic exchange effects [2]. We have used path integral techniques to investigate these systems and predict their spectroscopic behaviour in the microwave and the infrared regions of the spectrum. We are particularly interested in observing the superfluid response in clusters where the helium atoms have been substituted with parahydrogen molecules. Molecular hydrogen has been suggested as a potential candidate for the observation of superfluid response but this substance crystallizes before reaching a temperature low enough for superfluidity to appear. We will show theoretical and experimental results of a molecular superfluid response at the nanoscale via the formation of doped hydrogen clusters with a carbon dioxide probe molecule [3]. Properties such as density distributions, spectroscopic features, and effective rotational inertia can be extracted from the simulations. We will show new results for the case of asymmetric top molecules embedded in superfluid para-hydrogen clusters. A perspective on the current challenges of the field will be presented. [1] Grebenev, Toennies, and Vilesov, Science 279, 2083 (1998); Toennies and Vilesov, Angew. Chem.-Int. Edit. 43, 2622-2648 (2004). [2] Tang, Xu, McKellar and JÃ¤ger, Science 297, 2030 (2002) [3] Li, Le Roy, Roy, and McKellar, Phys. Rev. Lett. 105, 133401 (2010)


Motivation
Experiments on helium droplets and clusters
Important observable: B constant
J=1
2B
J=0
T=0.37 K
OC³²S in seeded beams
OC³²S in ⁴He droplets
OC³²S in ³He droplets
P(3)
P(2)
P(1)
R(0)
R(1)
R(2)
R(3)
a)
b)
c)
Relative Signal [%]
Relative Depletion [%]
2061.0
2062.0
2063.0
Laser Frequency [cm⁻¹]
Grebenev, Toennies, and Vilesov, Science 279, 2083 (1998); Toennies and Vilesov, Angew. Chem.-Int. Edit. 43, 2622-2648 (2004).
Rotational constant, B (MHz)
6000
5000
4000
3000
2000
1000
0
experimental nanodroplet value
0 1 2 3 4 5 6 7 8 9 10 11 12
Number of solvating He atoms, N
J. Tang, Y. Xu, A. R. W. McKellar and W. Jäger, Science 297, 2030 (2002)

Motivation

- Experiments on helium droplets and clusters
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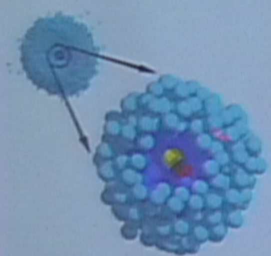
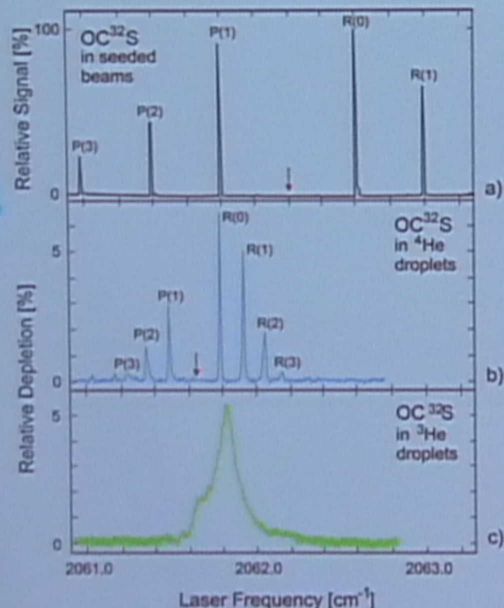
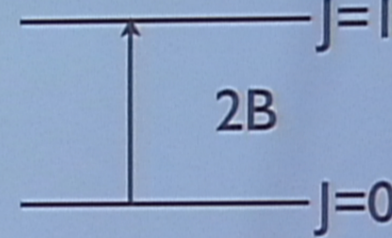
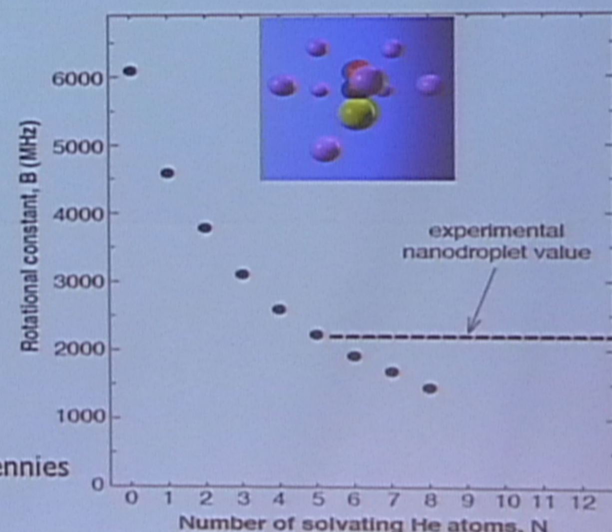




T=0.37 K





Grebenev, Toennies, and Vilesov, *Science* **279**, 2083 (1998); Toennies and Vilesov, *Angew. Chem.-Int. Edit.* **43**, 2622-2648 (2004).

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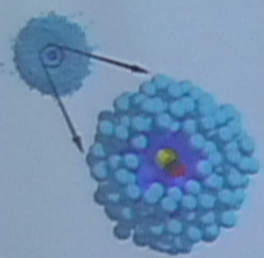
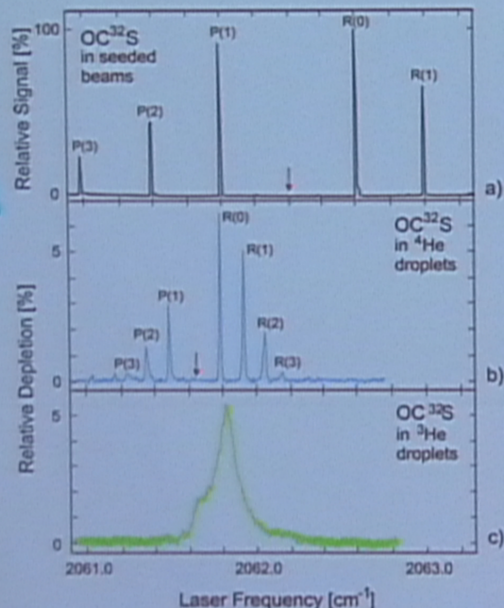
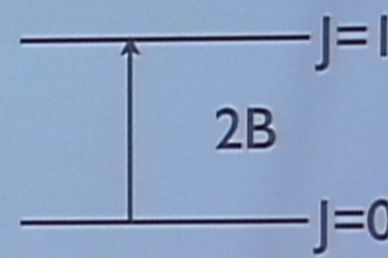
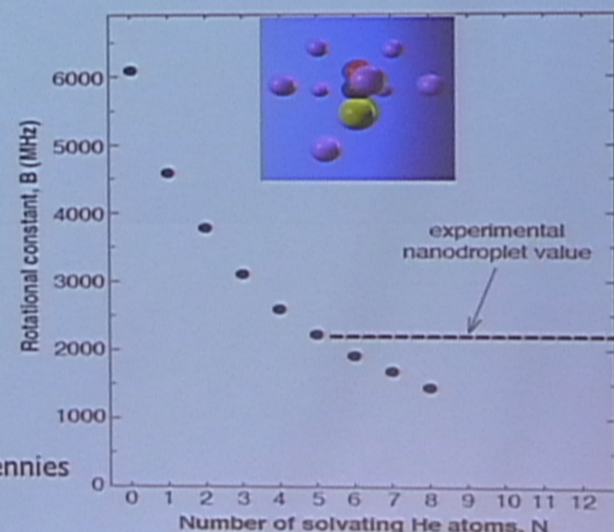




T=0.37 K





Grebenev, Toennies, and Vilesov, *Science* **279**, 2083 (1998); Toennies and Vilesov, *Angew. Chem.-Int. Edit.* **43**, 2622-2648 (2004).

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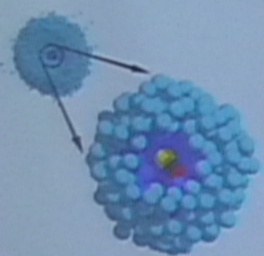
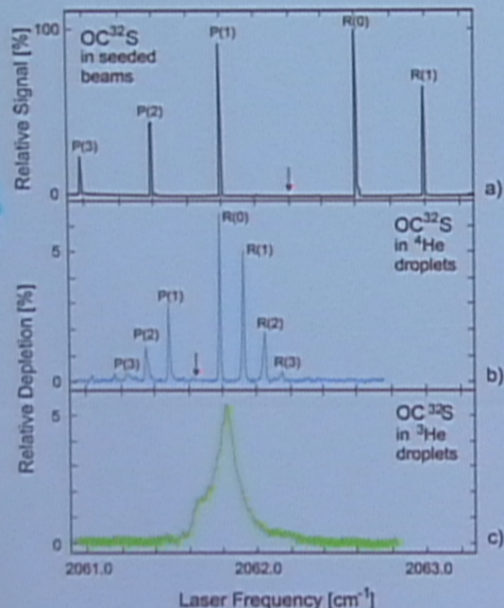
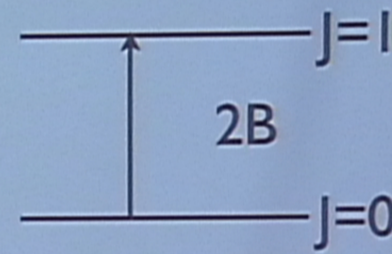
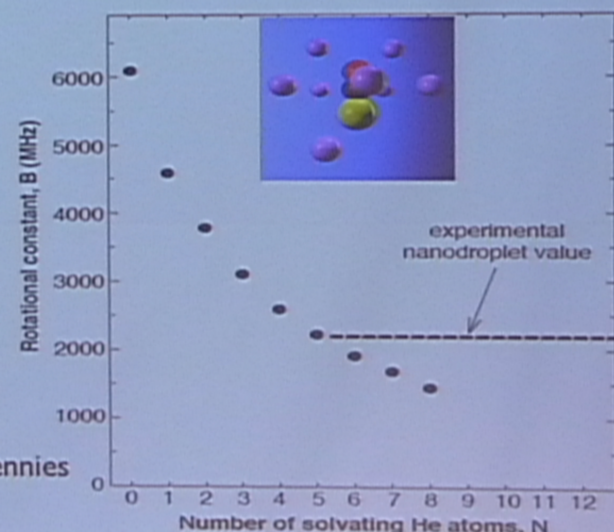


T=0.37 K







Grebenev, Toennies, and Vilesov, *Science* **279**, 2083 (1998); Toennies and Vilesov, *Angew. Chem.-Int. Edit.* **43**, 2622-2648 (2004).

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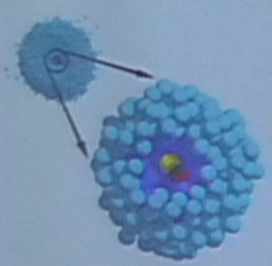

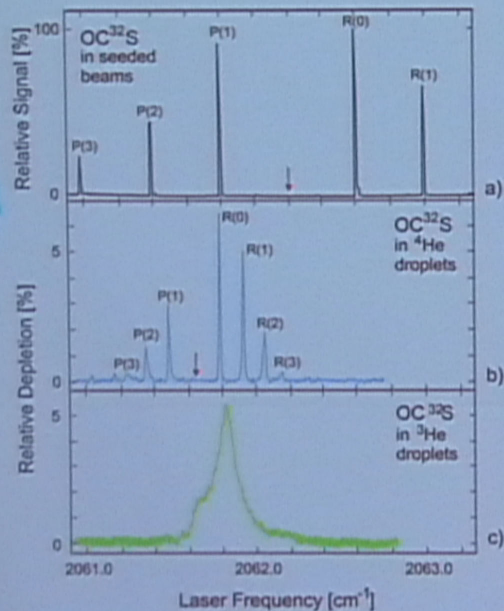

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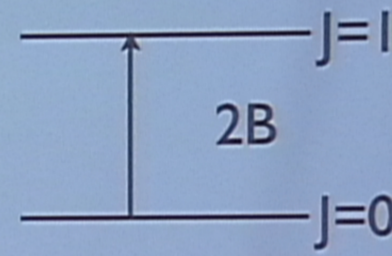
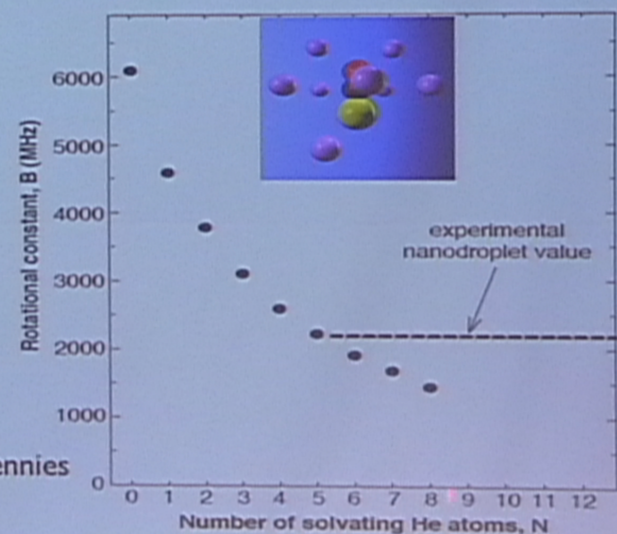
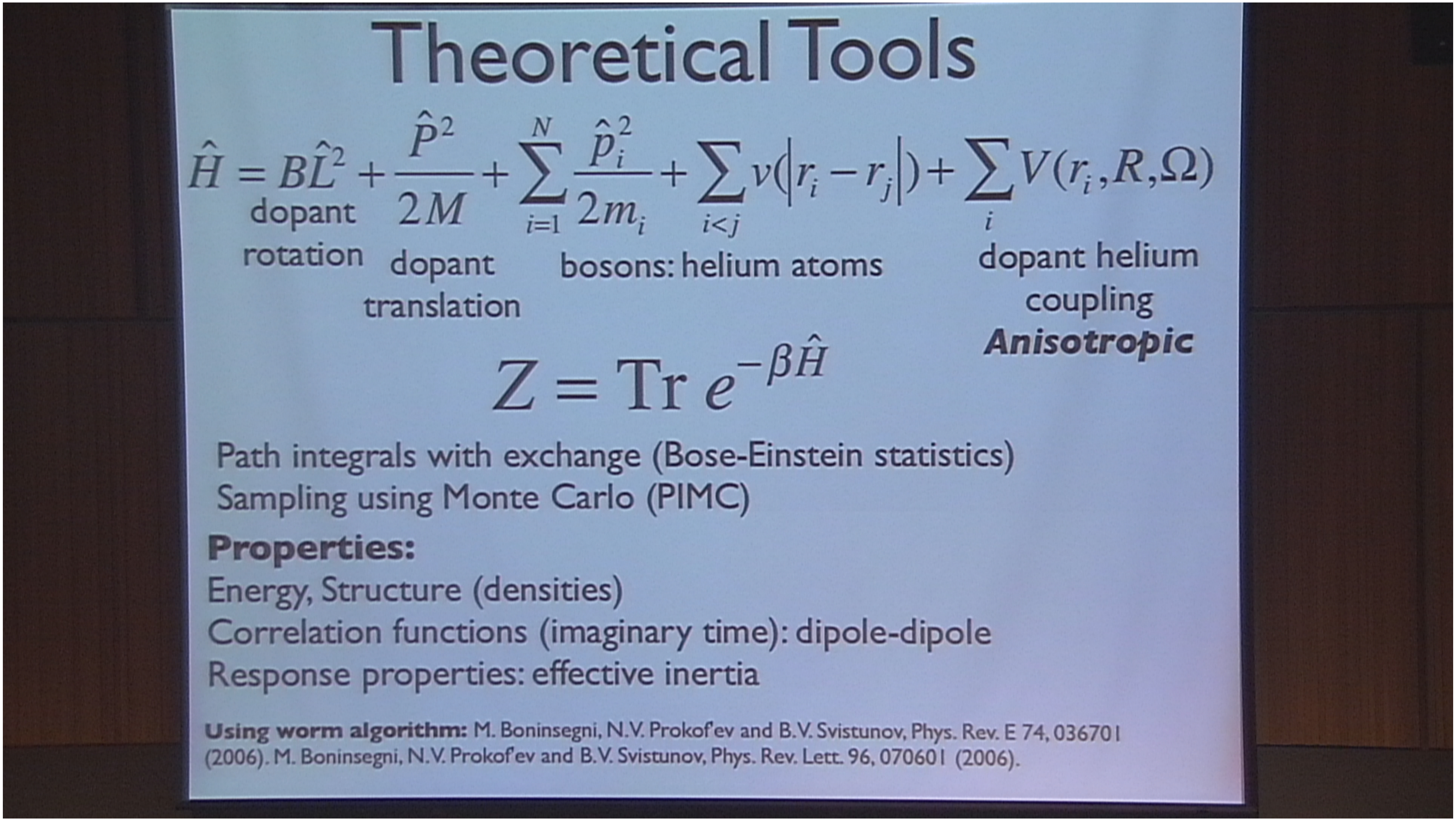
Grebenev, Toennies, and Vilesov, *Science* **279**, 2083 (1998); Toennies and Vilesov, *Angew. Chem.-Int. Edit.* **43**, 2622-2648 (2004).





J. Tang, Y. Xu, A. R. W. McKellar and W. Jäger, Science **297**, 2030 (2002)


Theoretical Tools
$\hat{H} = B\hat{L}^2 + \frac{\hat{P}^2}{2M} + \sum_{i=1}^{N} \frac{\hat{p}_i^2}{2m_i} + \sum_{i<j} v(|r_i - r_j|) + \sum_i V(r_i, R, \Omega)$
dopant rotation
dopant translation
bosons: helium atoms
dopant helium coupling
Anisotropic
$Z = \mathrm{Tr}\, e^{-\beta \hat{H}}$
Path integrals with exchange (Bose-Einstein statistics)
Sampling using Monte Carlo (PIMC)
Properties:
Energy, Structure (densities)
Correlation functions (imaginary time): dipole-dipole
Response properties: effective inertia
Using worm algorithm: M. Boninsegni, N.V. Prokof'ev and B.V. Svistunov, Phys. Rev. E 74, 036701 (2006). M. Boninsegni, N.V. Prokof'ev and B.V. Svistunov, Phys. Rev. Lett. 96, 070601 (2006).

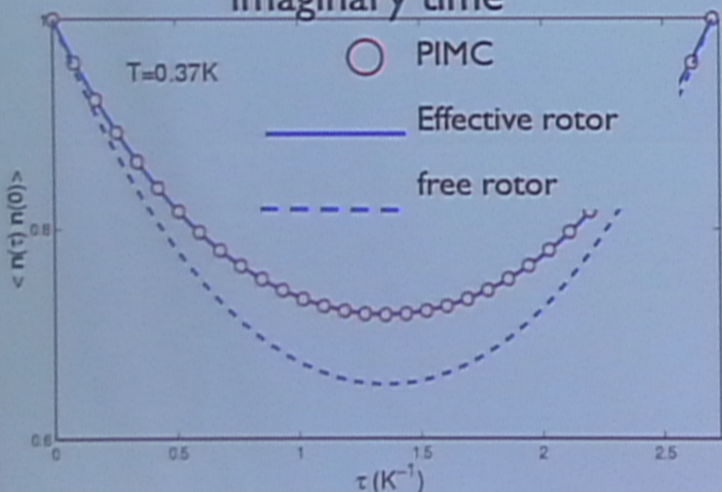
Can we obtain spectral features?

Rotational spectrum: Fourier transform of the real time dipole auto-correlation function (difficult to calculate for large systems)

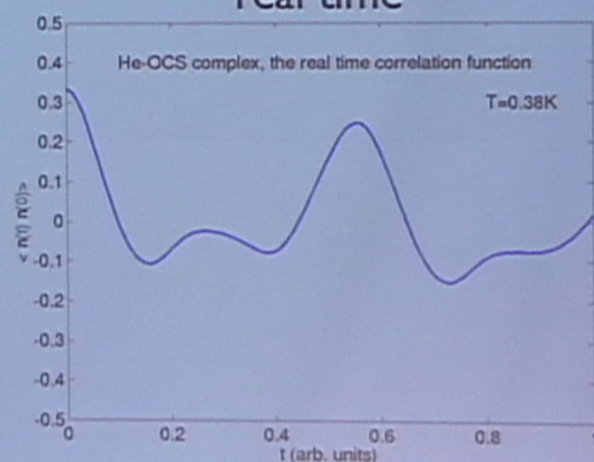
We opt for its imaginary time counterpart and ***model*** fit:

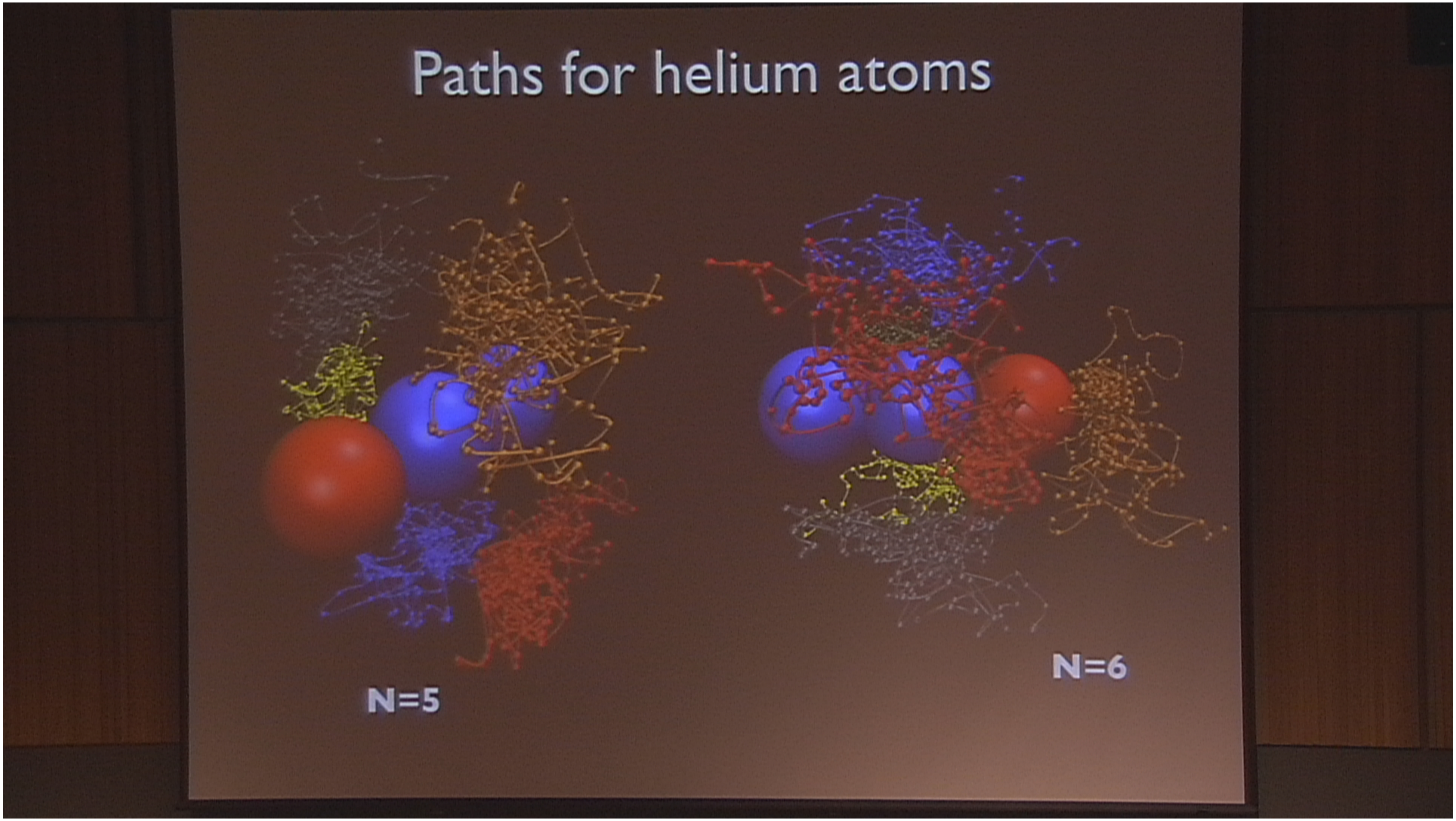
$$\langle \hat{\mathbf{n}}(\tau) \cdot \hat{\mathbf{n}}(0) \rangle = \frac{1}{Z} \mathrm{Tr} \left\{ e^{-\beta \hat{H}} e^{\tau \hat{H}} \hat{\mathbf{n}}\, e^{-\tau \hat{H}} \cdot \hat{\mathbf{n}} \right\}$$

imaginary time

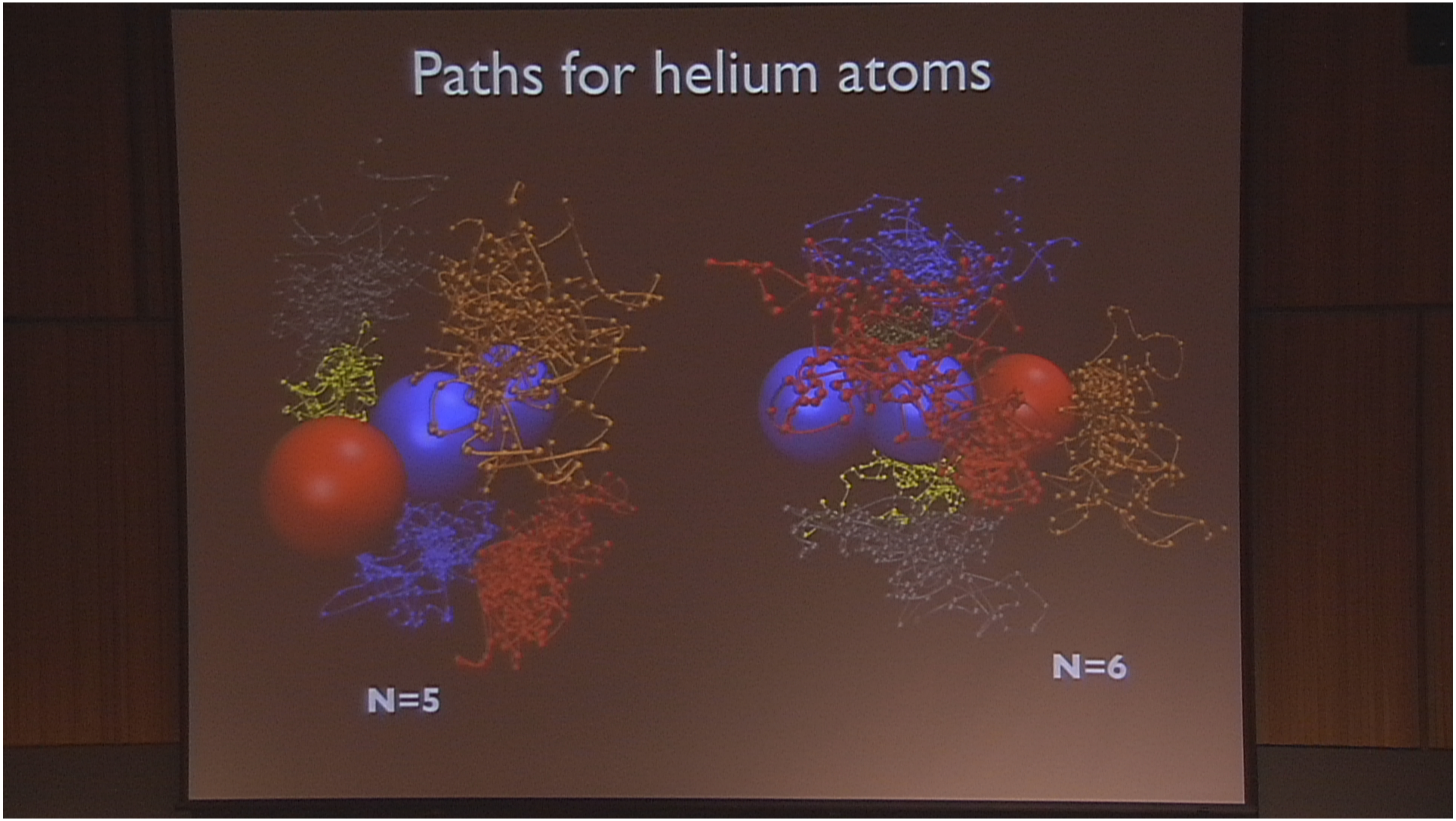


real time





Paths for helium atoms
N=5
N=6


Paths for helium atoms
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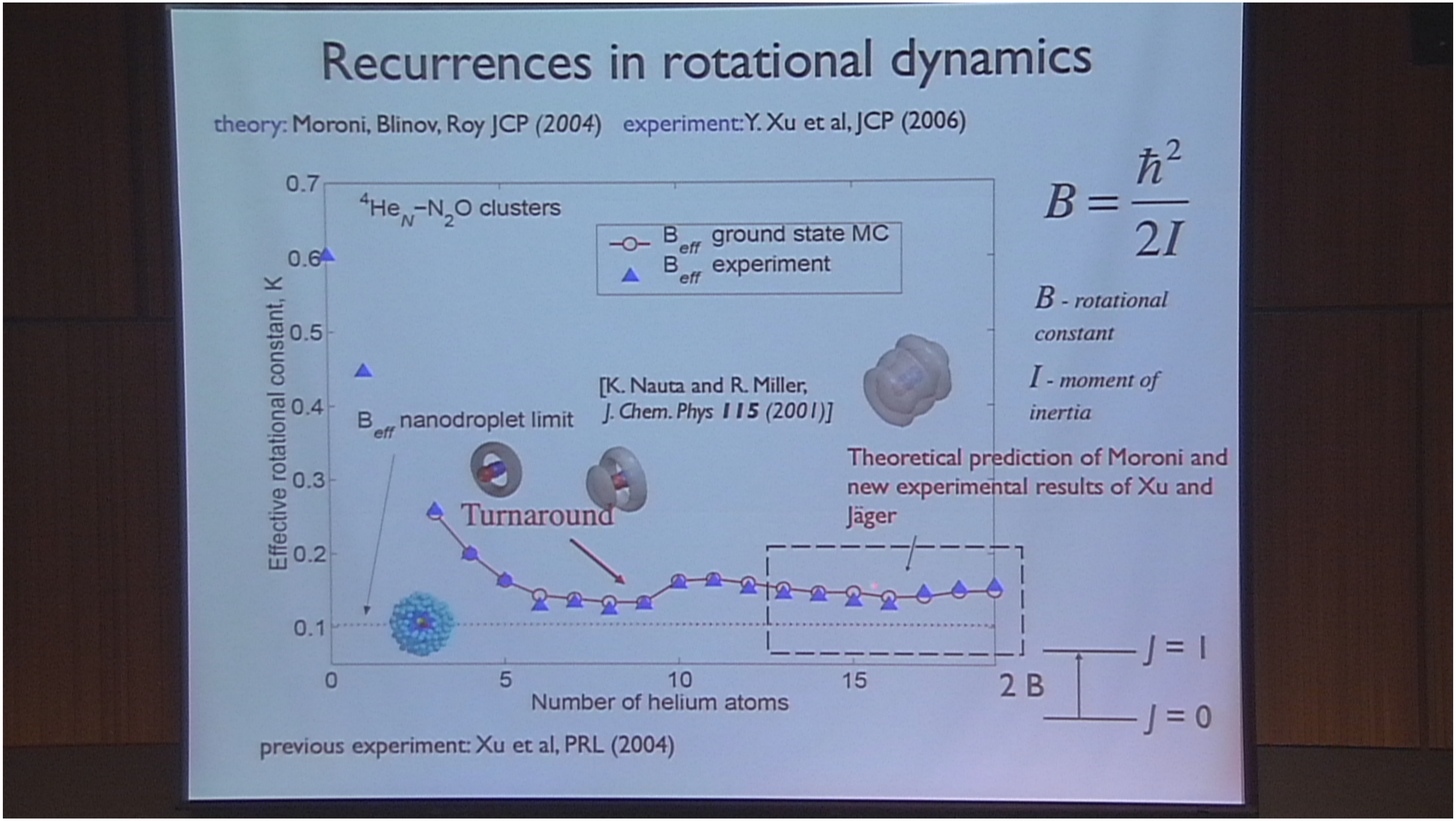
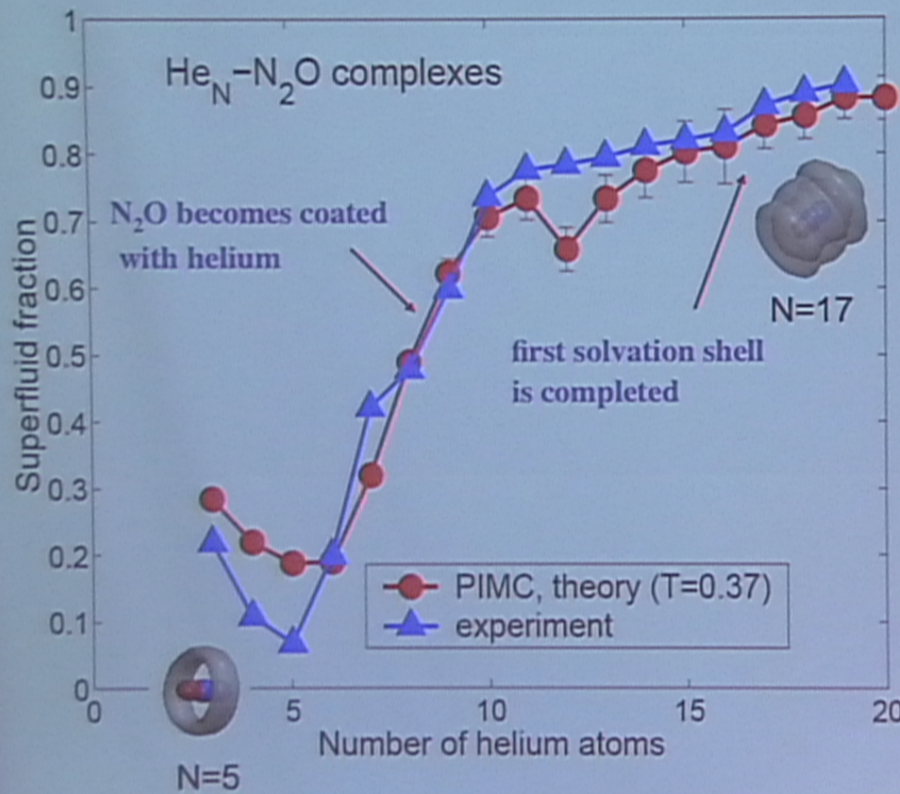

Recurrences in rotational dynamics
theory: Moroni, Blinov, Roy JCP (2004) experiment: Y. Xu et al, JCP (2006)
$B = \frac{\hbar^2}{2I}$
B - rotational constant
I - moment of inertia
$^4He_N-N_2O$ clusters
B_{eff} ground state MC
B_{eff} experiment
Effective rotational constant, K
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
5
10
15
Number of helium atoms
B_{eff} nanodroplet limit
[K. Nauta and R. Miller, J. Chem. Phys 115 (2001)]
Turnaround
Theoretical prediction of Moroni and new experimental results of Xu and Jäger
2 B
J = 1
J = 0
previous experiment: Xu et al, PRL (2004)

Proposal: dopant molecule as a probe of superfluidity at the microscopic level



Superfluid fraction:

$$f_s = 1 - \frac{I_n}{I_o}$$

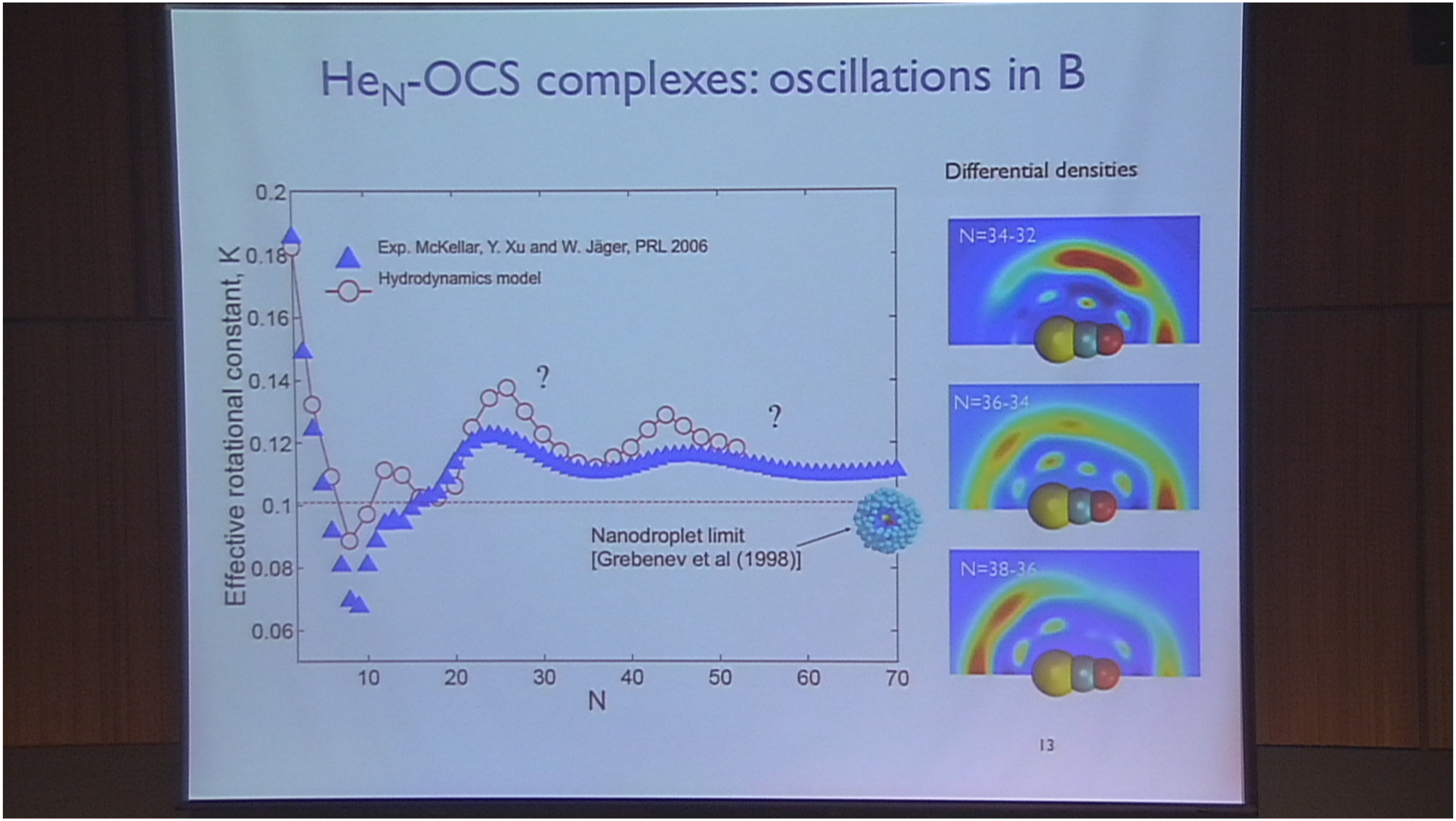
with I_n deduced from spectroscopic experiments:

$$I_n = \frac{\hbar^2}{2B} - I^{imp}$$

and I_o obtained from MC calculations:

$$I_o = \int \rho_{total} r_\perp^{\,2} dV$$

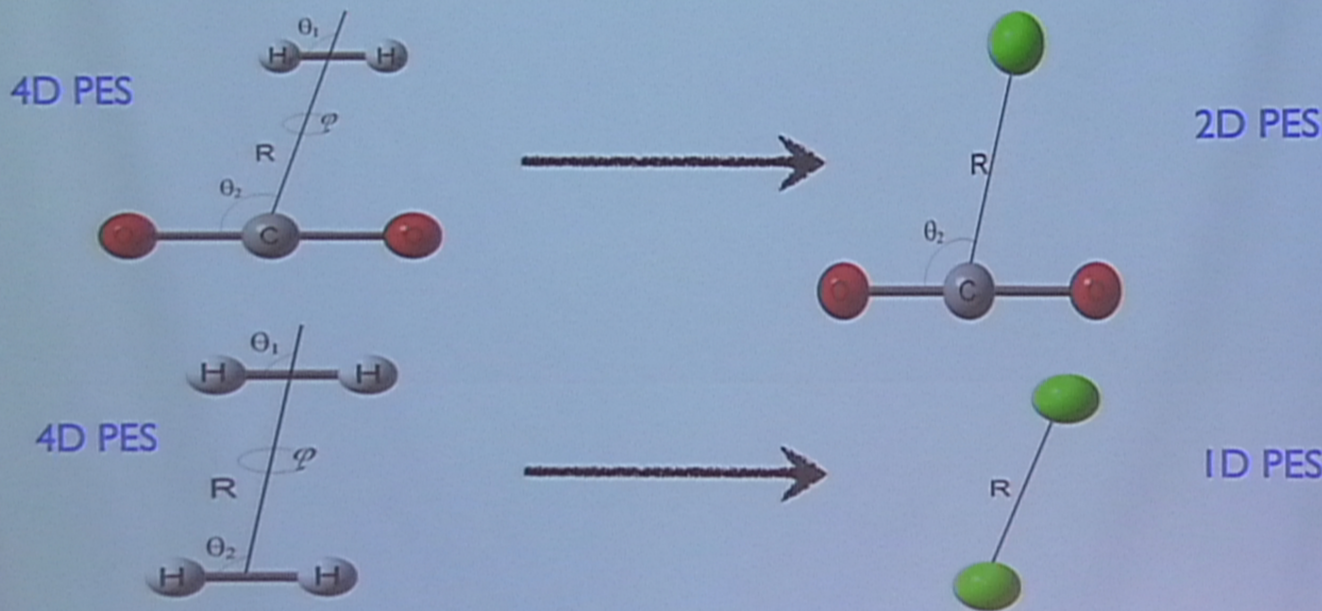
Xu, Blinov, Jager, Roy JCP (2006)


He_N-OCS complexes: oscillations in B
Differential densities
Exp. McKellar, Y. Xu and W. Jäger, PRL 2006
Hydrodynamics model
Effective rotational constant, K
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
10
20
30
40
50
60
70
N
?
?
Nanodroplet limit
[Grebenev et al (1998)]
N=34-32
N=36-34
N=38-36
13

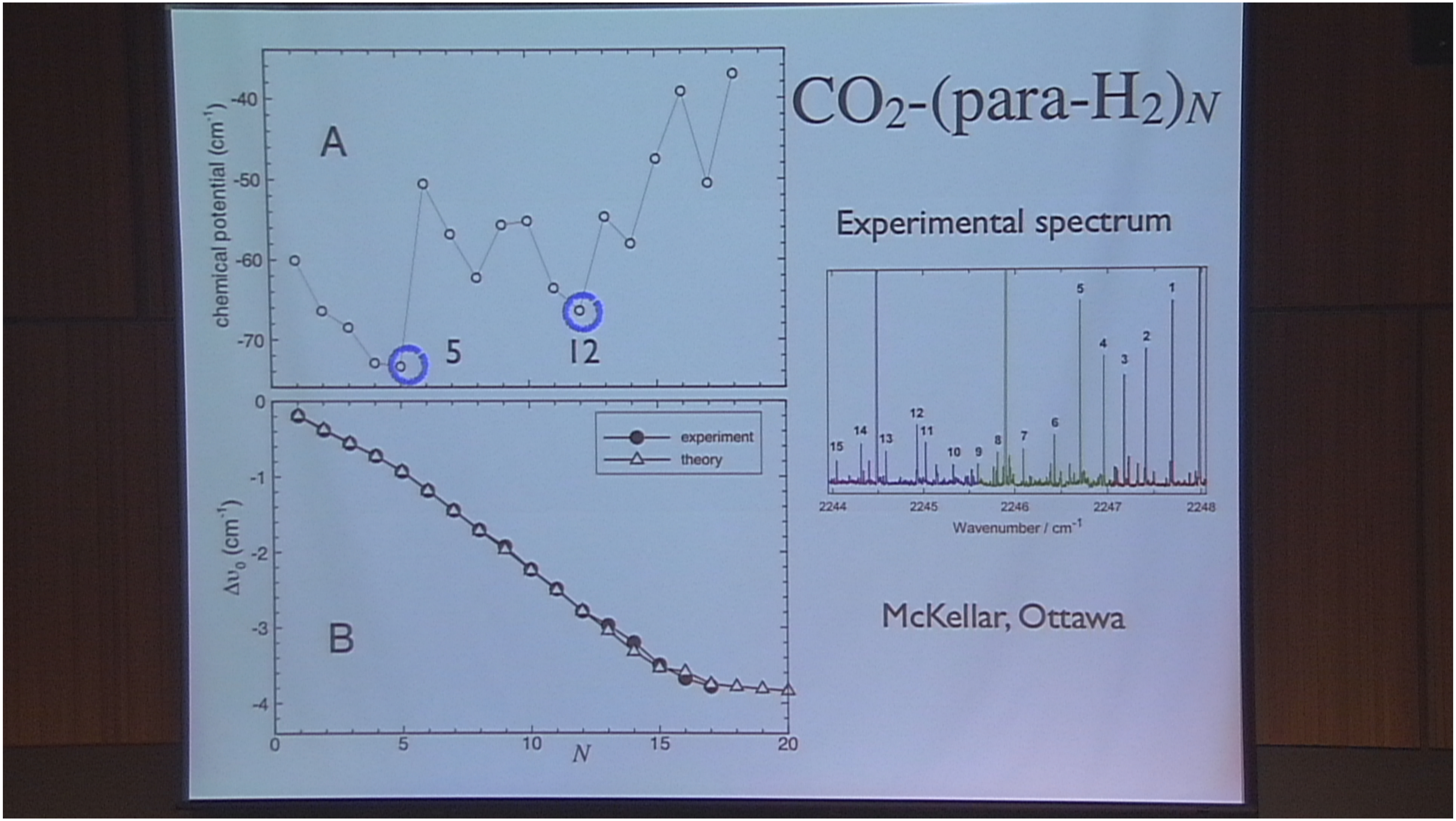
Reduced Dimension PES

Rotational constant CO_2 vs. H_2:

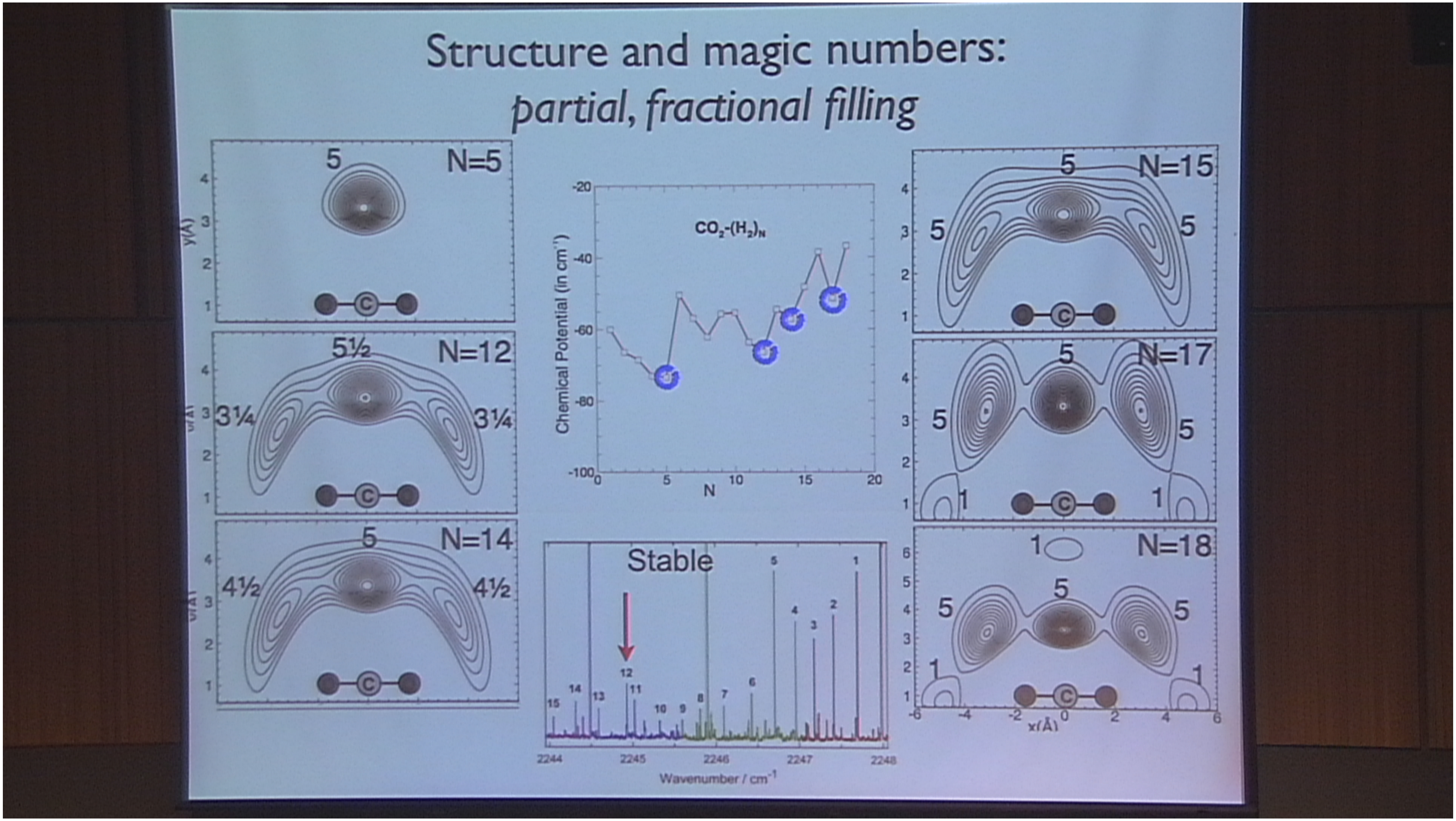
$$\frac{B_{H_2}}{B_{CO_2}} = \frac{59.322}{0.390} \approx 152$$



Li, Roy, and Le Roy, J. Chem. Phys. *J. Chem. Phys.* **132**, 214309 (2010); *ibid* **133**, 104305 (2010).



CO2-(para-H2)N
A
B
5
12
chemical potential (cm-1)
experiment
theory
N
Experimental spectrum
Wavenumber / cm-1
McKellar, Ottawa


Structure and magic numbers:
partial, fractional filling
N=5
N=12
N=14
N=15
N=17
N=18
CO2-(H2)N
Chemical Potential (in cm-1)
N
Stable
Wavenumber / cm-1
x(Å)
y(Å)

$$B_{\text{classical}} = \frac{\hbar^2}{2(I_{CO_2} + I^{H_2}_{\text{classical}})}$$

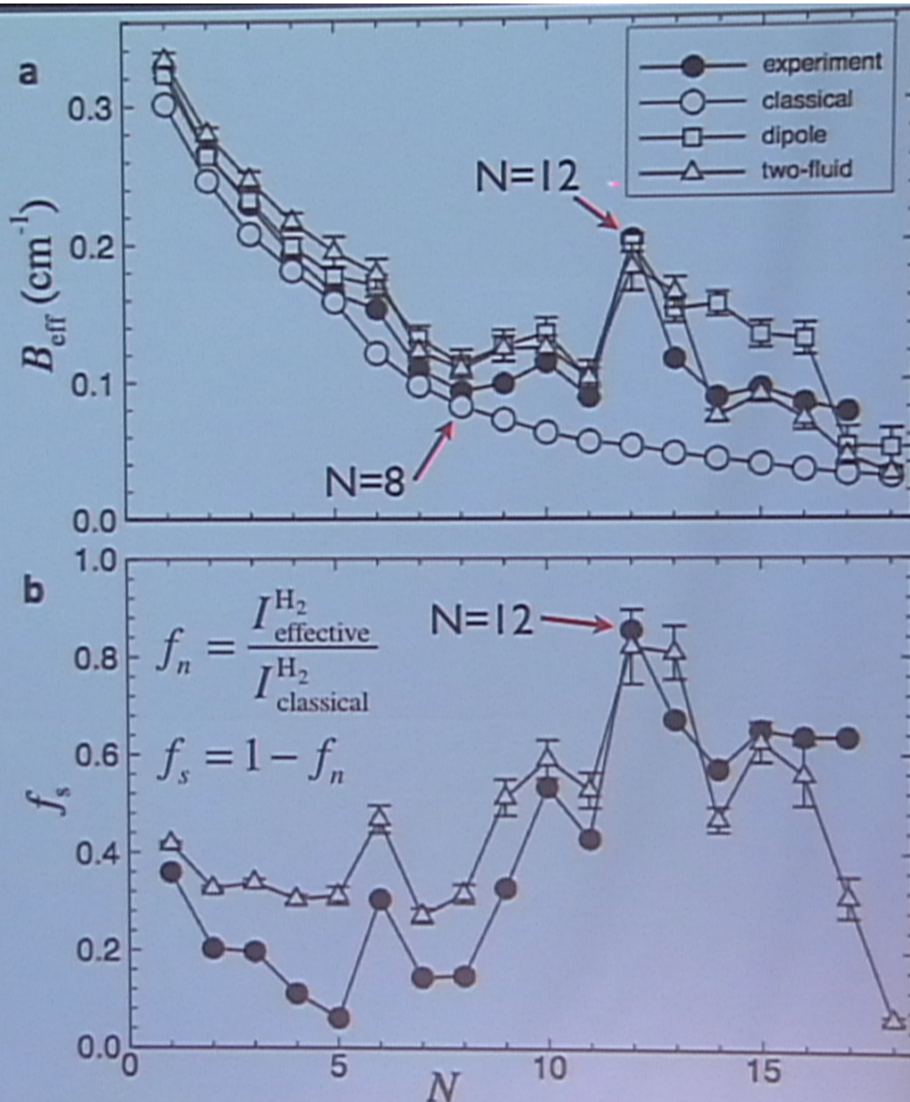
$$B_{\text{two fluid}} = \frac{\hbar^2}{2(I_{CO_2} + I^{H_2}_{\text{effective}})}$$

$$\frac{I^{H_2}_{\text{effective}}\omega^2}{2} = F_\omega$$

$$I^{H_2}_{\text{effective}} = \frac{\partial^2 F_\omega}{\partial \omega^2}$$

$$F_\omega = -k_B T \ln Z_\omega$$

N=12 Maximum corresponds to global fractional filling



Conclusions

- Confirmed superfluid response to probe rotation in doped para-H_2 clusters
- Turnaround in *B* constants is a direct sign of the onset of decoupling
- First experimental determination of superfluid fraction in a ***molecular*** superfluid. Theory was necessary to interpret this experiment.
- But superfluid response seems to die out as *N* increases because of solidification

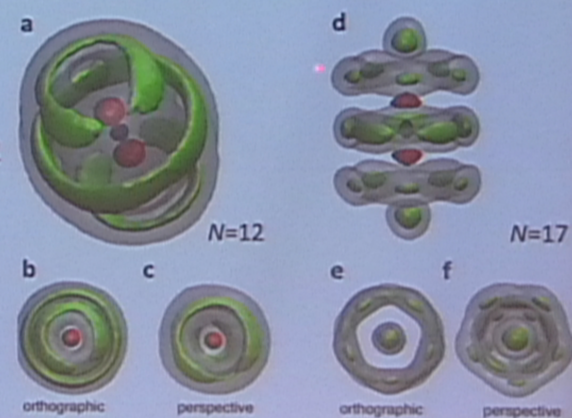
PRL 105, 133401 (2010) PHYSICAL REVIEW LETTERS week ending 24 SEPTEMBER 2010

Molecular Superfluid: Nonclassical Rotations in Doped *Para*-Hydrogen Clusters

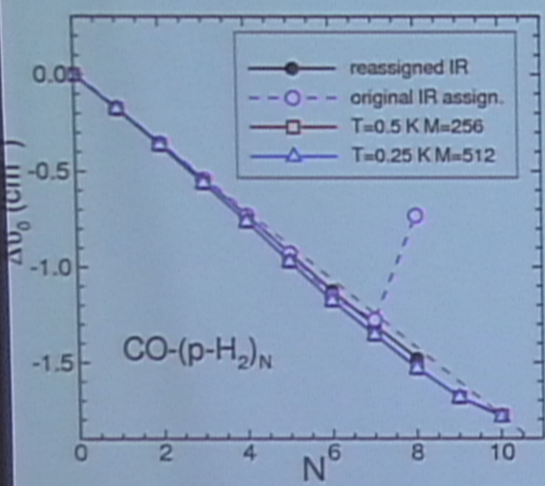
Hui Li,[1,2] Robert J. Le Roy,[1] Pierre-Nicholas Roy,[1,*] and A. R. W. McKellar[3,†]
[1]*Department of Chemistry, University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada*
[2]*Institute of Theoretical Chemistry, State Key Laboratory of Theoretical and Computational Chemistry, Jilin University, 2519 Jiefang Road, Changchun 130023, People's Republic of China*
[3]*Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada*

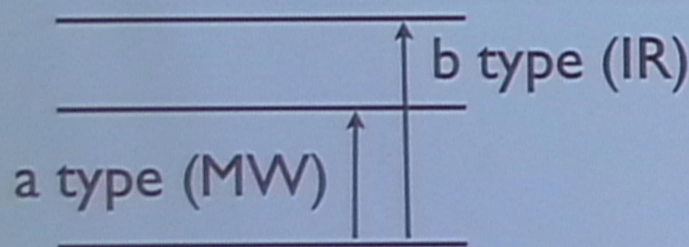
(Received 21 April 2010; published 23 September 2010)

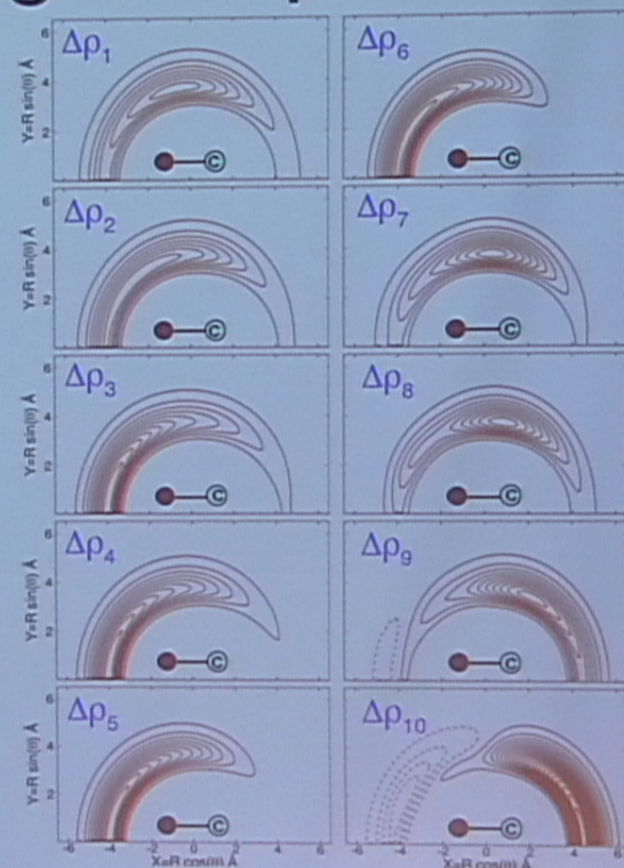
Clusters of *para*-hydrogen (pH_2) have been predicted to exhibit superfluid behavior, but direct observation of this phenomenon has been elusive. Combining experiments and theoretical simulations, we have determined the size evolution of the superfluid response of pH_2 clusters doped with carbon dioxide (CO_2). Reduction of the effective inertia is observed when the dopant is surrounded by the pH_2 solvent. This marks the onset of molecular superfluidity in pH_2. The fractional occupation of solvation rings around CO_2 correlates with enhanced superfluid response for certain cluster sizes.



CO, a lighter and gentler probe

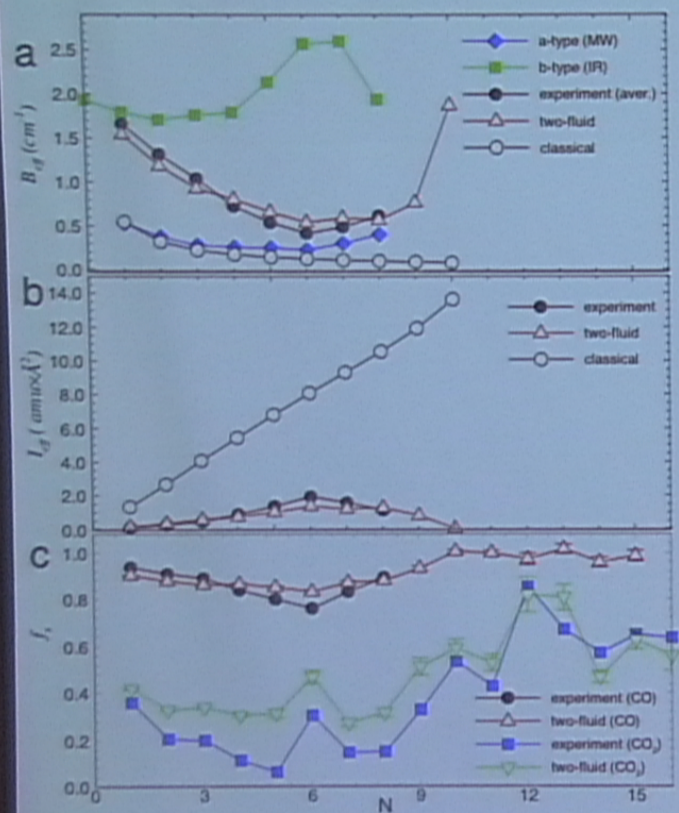






Raston, Jager, Li, Le Roy, and Roy, *Phys. Rev. Lett., accepted*

A persistent molecular superfluid response



$$H = H_0 - \mu_z E_z \cos\alpha$$

perturbation theory

$$\Delta E_0^{(2)} = -\sum_n \frac{\left|\langle 0|\cos\alpha|n\rangle\right|^2 \mu_z^2 E_z^2}{E_n - E_0}$$

$$\Delta E_0^{(2)} = \frac{-\mu_z^2 E_z^2}{6B}$$ linear rotor model

$$I_{eff} = \frac{-3\hbar^2}{\mu_z^2 E_z^2} \Delta E_0^{(2)}$$ total effective inertia

$$I_{eff} = \sum_n \frac{3\left|\langle 0|\cos\alpha|n\rangle\right|^2 \hbar^2}{E_n - E_0}$$

$$I_{H_2} = I_{eff} - I_{CO}$$

New experimental estimator of f_s!

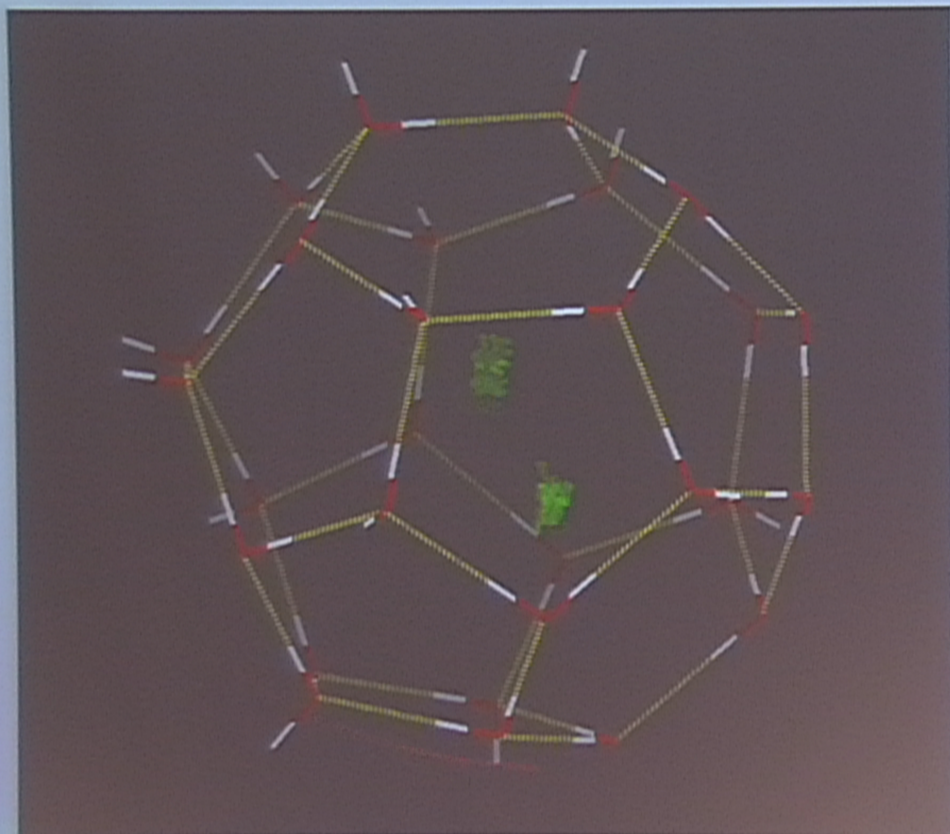
Raston, Jager, Li, Le Roy, and Roy, *Phys. Rev. Lett., accepted*

Beyond linear dopants?
Water

- a lighter and faster rotor
- asymmetric top molecule
- theoretical challenge and important coding work
- first PIMC simulation of a solvated asymmetric top with bosonic exchange for the environment.

Zeng, Li, and Roy, *Phys. Rev. Lett., submitted*

Many waters, a few hydrogens: clathrate hydrates



2 parahydrogen molecules in a water cage at 100K