Endofullerenes:

Nano-scale test tubes for single molecules and atoms

Malcolm Levitt
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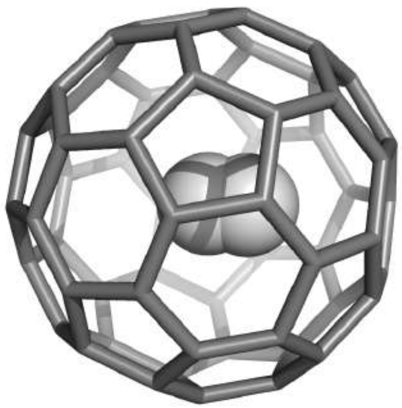
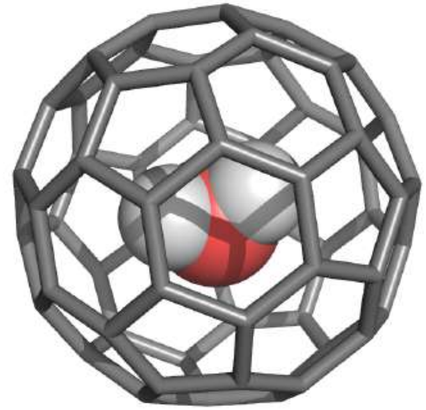
THE ROYAL SOCIETY
erc

Endofullerenes by organic synthesis





Encapsulation of Molecular Hydrogen in Fullerene C_{60} by Organic Synthesis

Koichi Komatsu,* Michihisa Murata, Yasujiro Murata

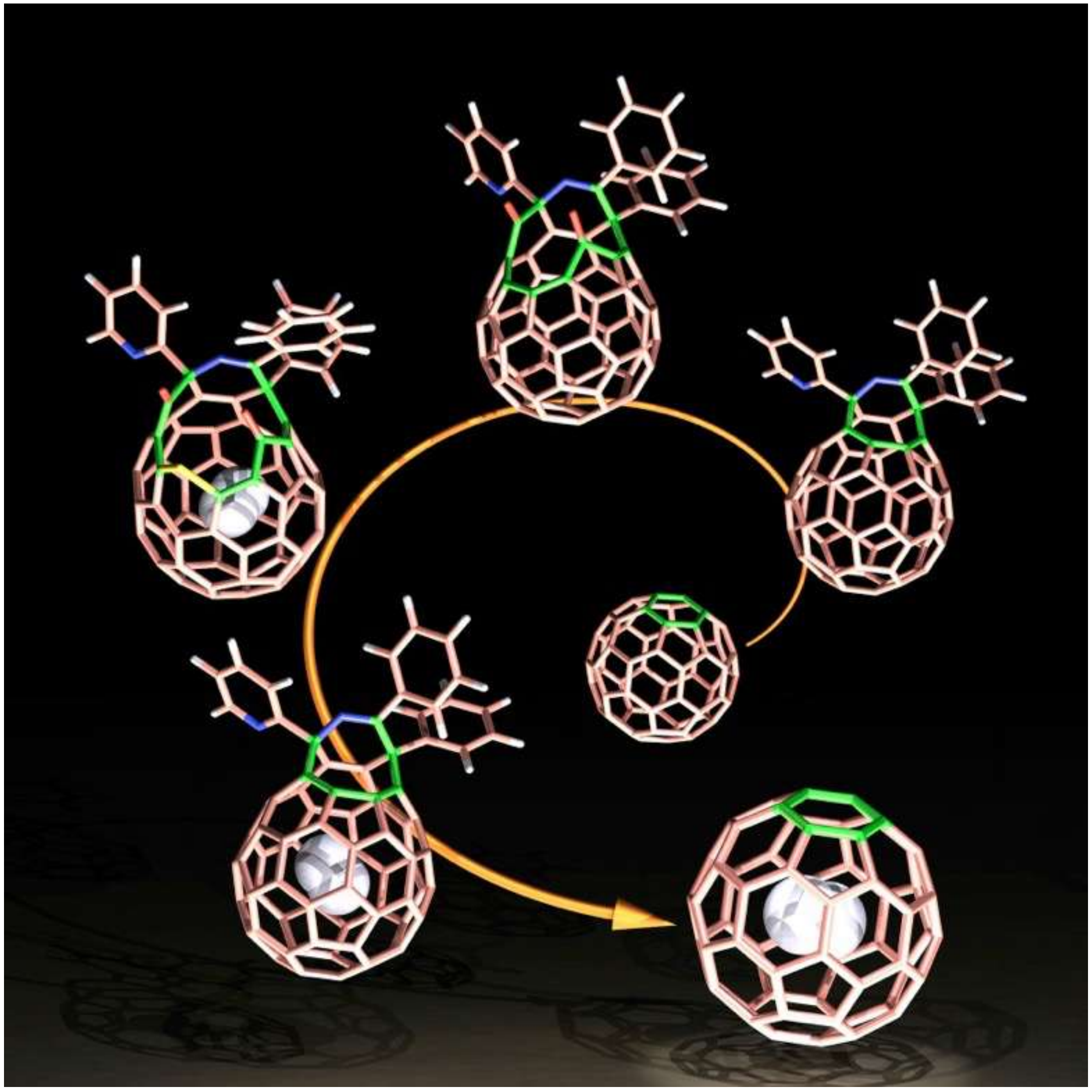
14 JANUARY 2005 VOL 307 SCIENCE

A Single Molecule of Water Encapsulated in Fullerene C_{60}

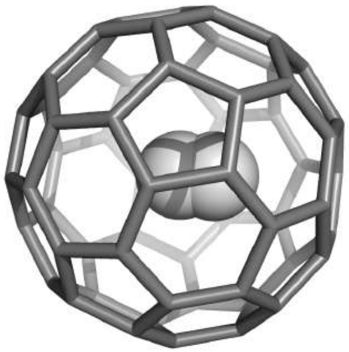
Kei Kurotobi and Yasujiro Murata*

SCIENCE VOL 333 29 JULY 2011

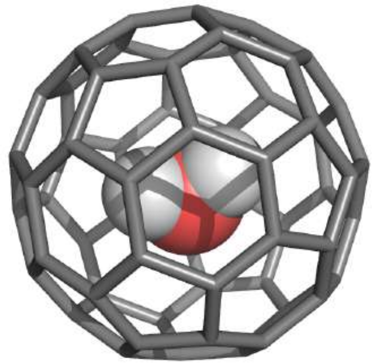
"Molecular surgery"



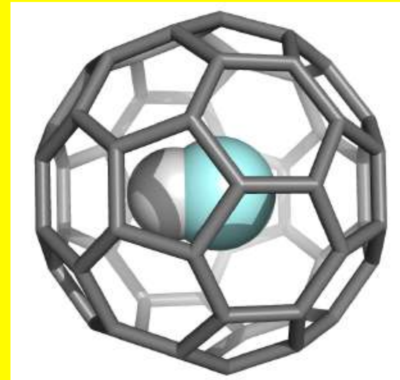
Yas Murata



H_2@C_{60}
HD@C_{60}
D_2@C_{60}



H_2O@C_{60}
D_2O@C_{60}
$H_2{}^{17}O$@C_{60}

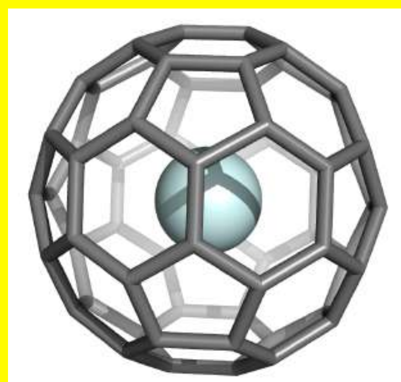


HF@C_{60}

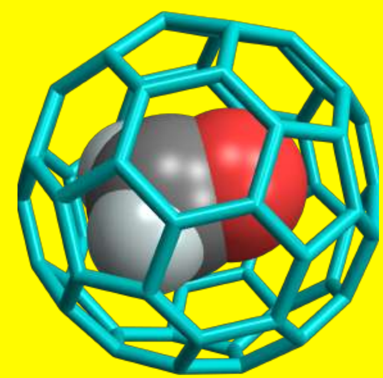
Richard Whitby

Nature Chem. (2016)
Angew. Chem. (2019)
Angew. Chem. (2021)
Nature Commun. (2024)

CH_4@C_{60}



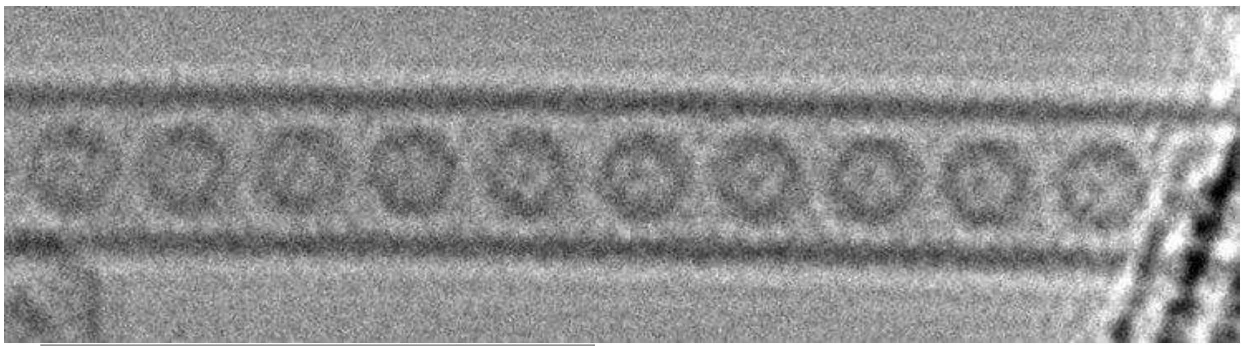
He@C_{60},
Ne@C_{60}...



CH_2O@C_{60}

Endofullerenes

- Symmetrical carbon cages encapsulating single molecules or atoms
- Stable black solids, purple solutions
- Highly pure and homogeneous
- May be studied from ~mK to ~500 K
- Available in macro quantities ~100mg
- May be functionalised, reacted, etc.



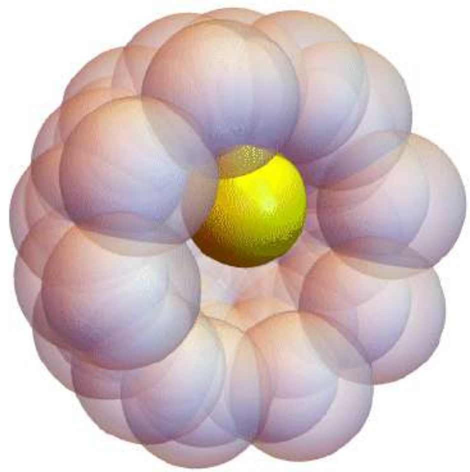
HF@C_{60} in SWCNT

Andrei Khlobystov

phenomena

- rotational quantization
- translational confinement
  - “particle-in-a-box” quantization
- translation-rotation coupling
- spin isomerism
  - metastable spin-isomer states
  - spin-isomer conversion

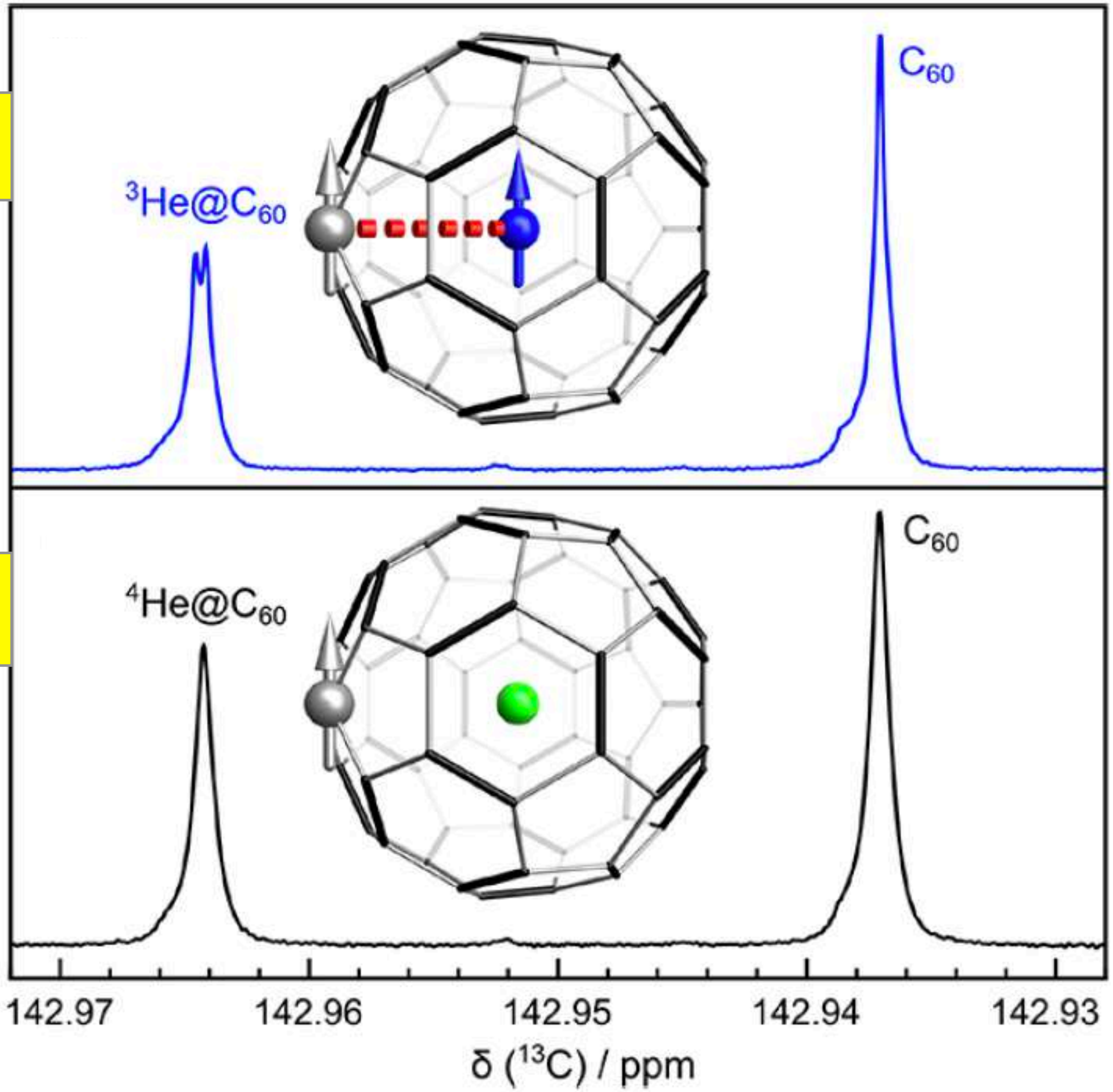
$He@C_{60}$



Solution ^{13}C NMR: $He@C_{60}$

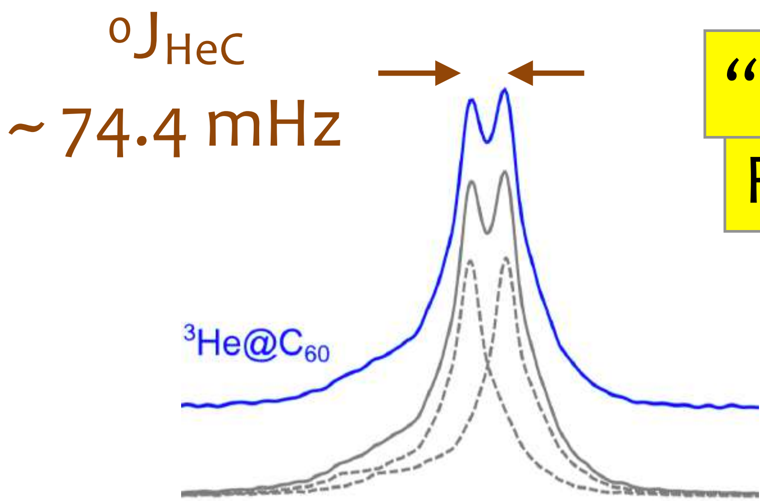
$^{3}He@C_{60}$

$^{4}He@C_{60}$



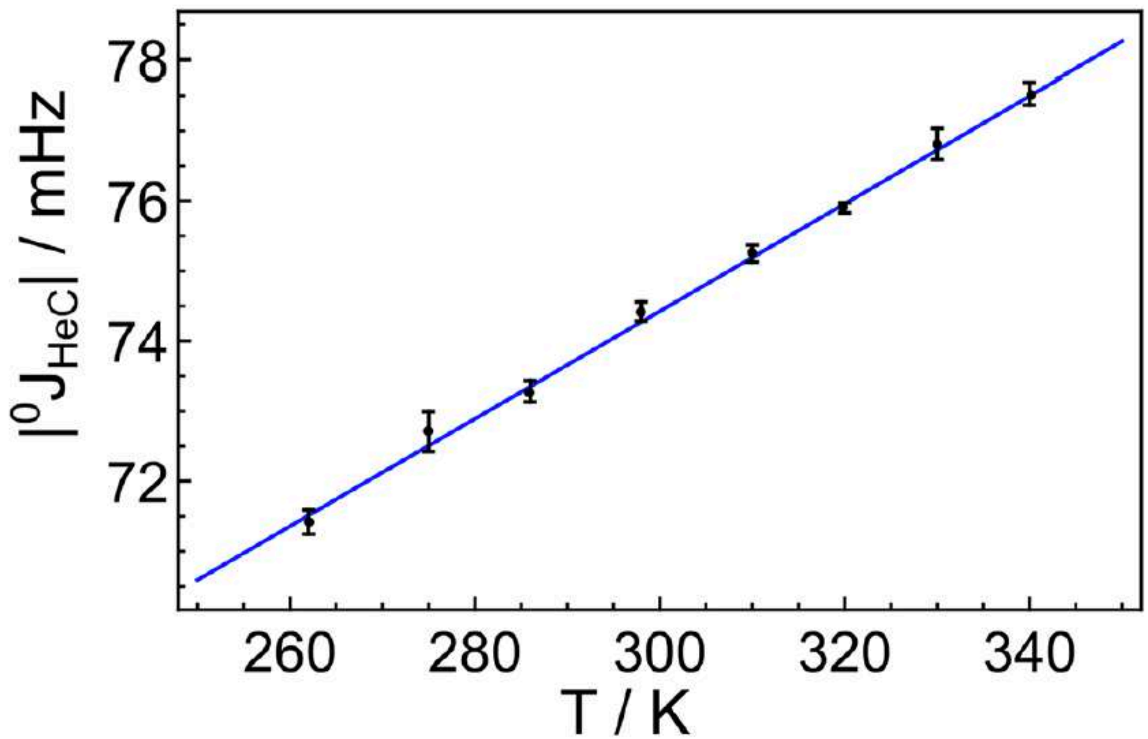
George Bacanu

Bacanu et al. JACS (2020)

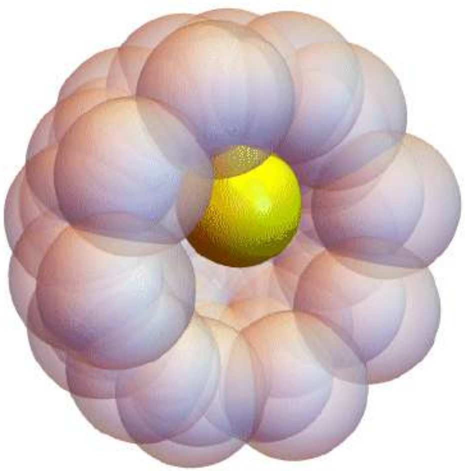


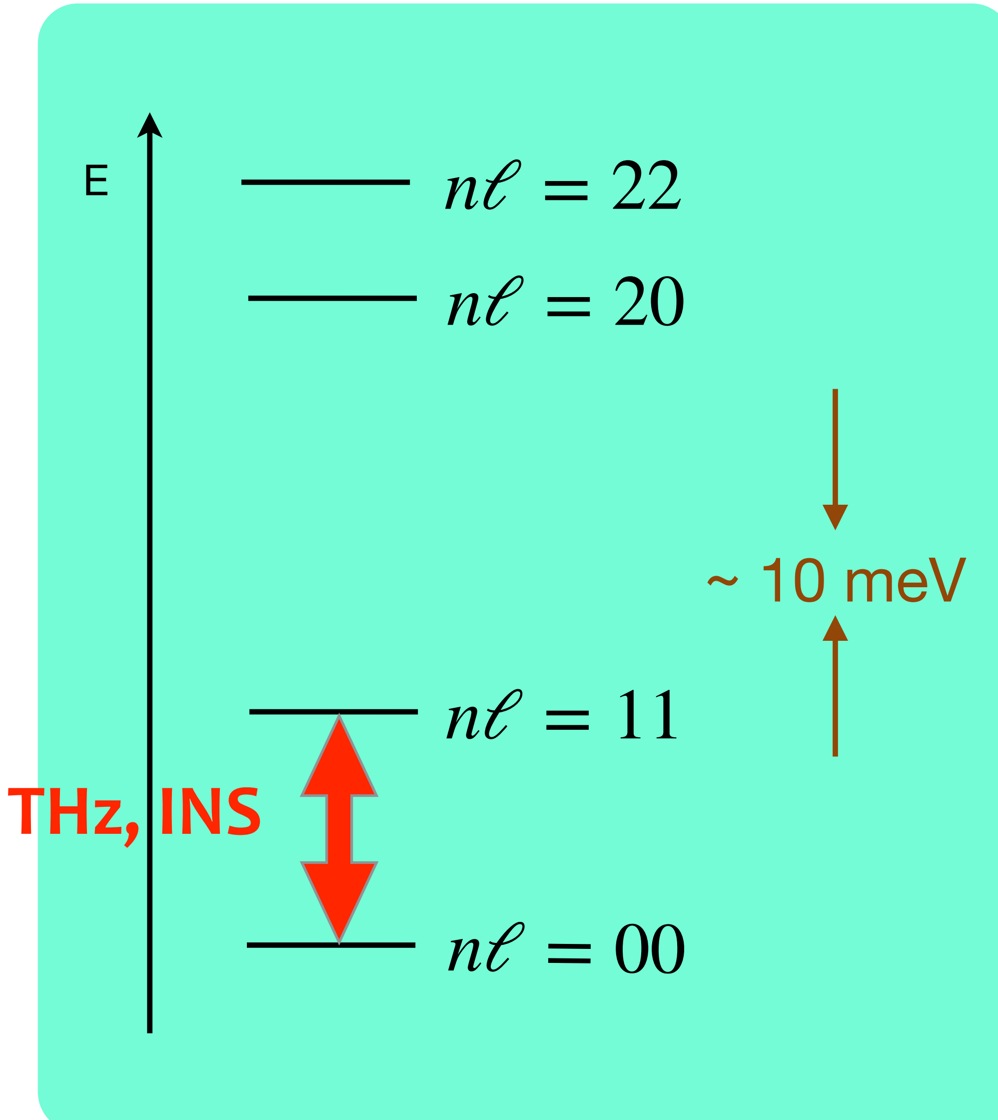
“Non-bonded” J-coupling

First observation of a J-coupling to ^{3}He

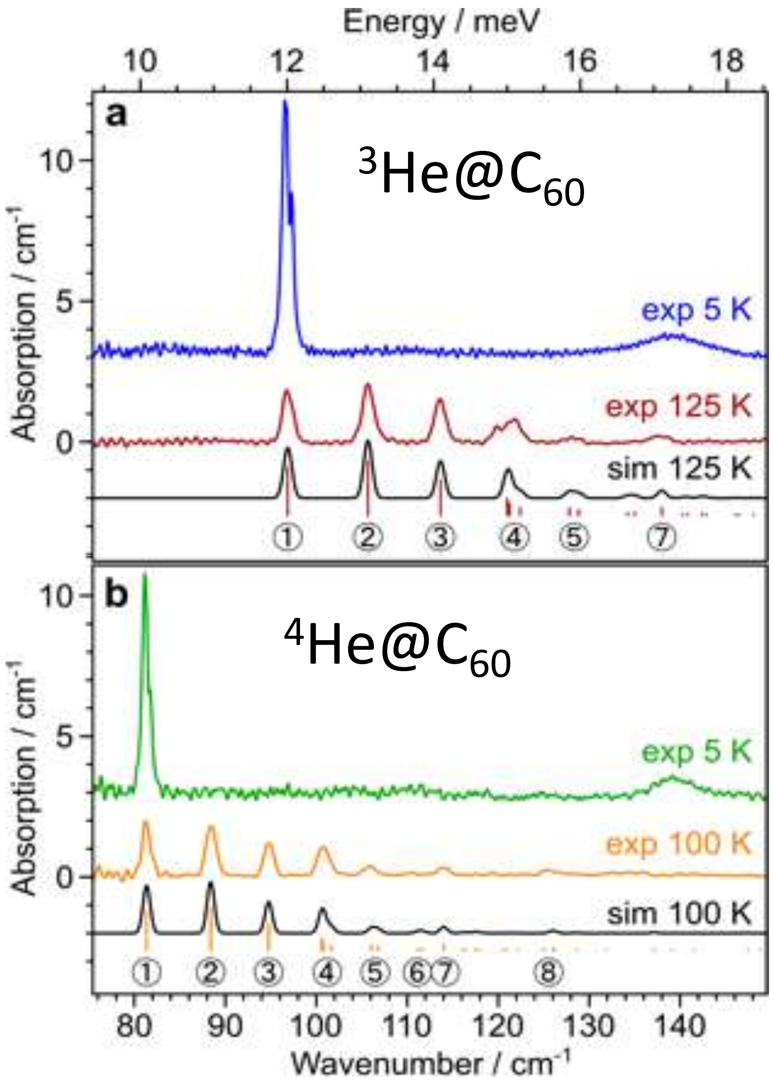


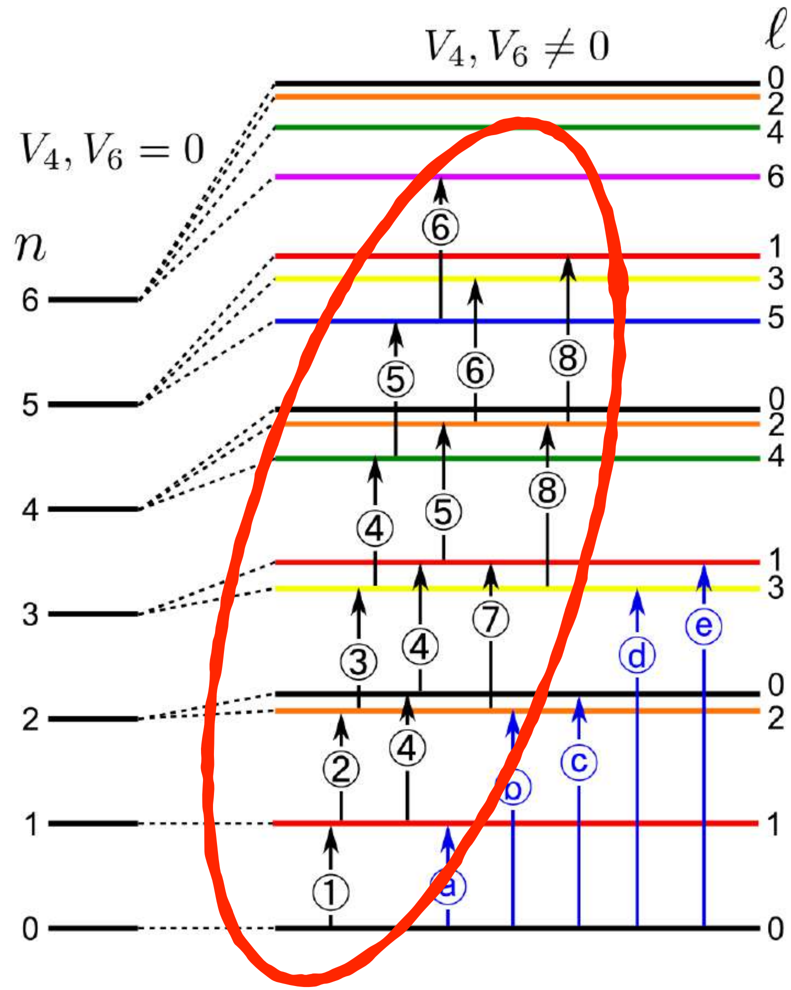
$He@C_{60}$: Spatial Quantisation





THz

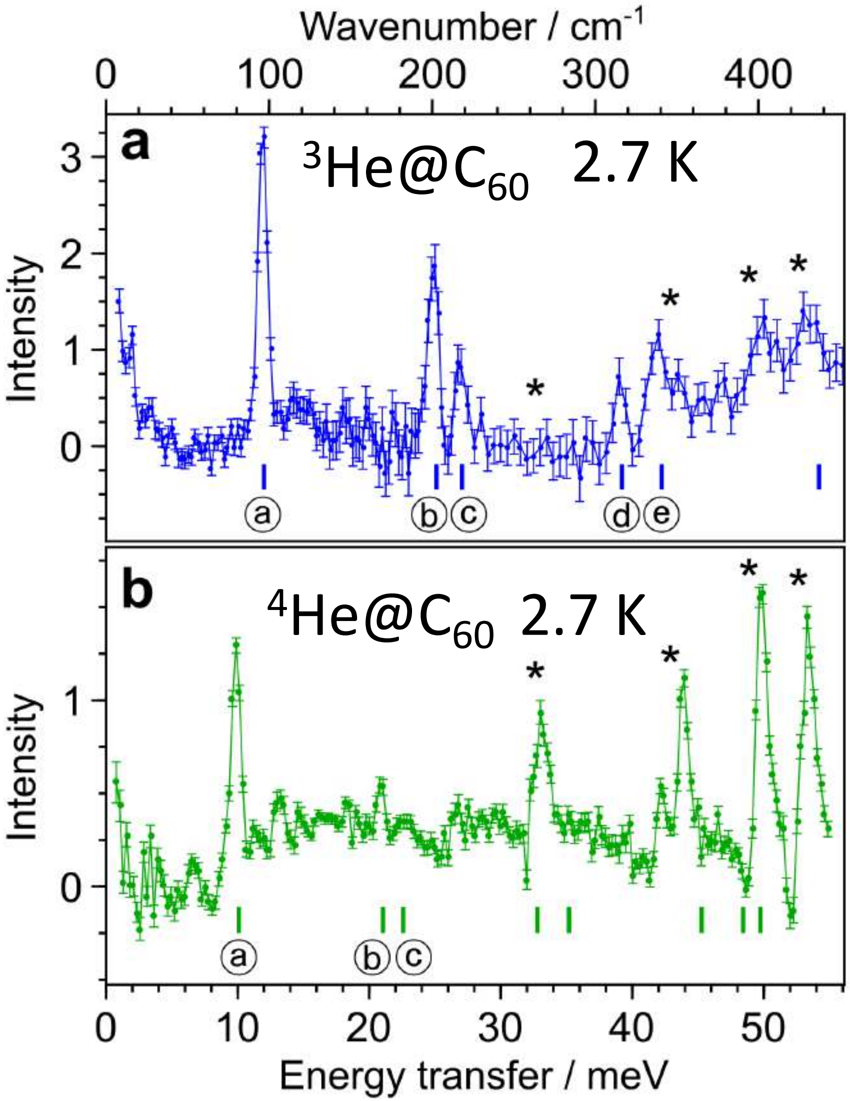


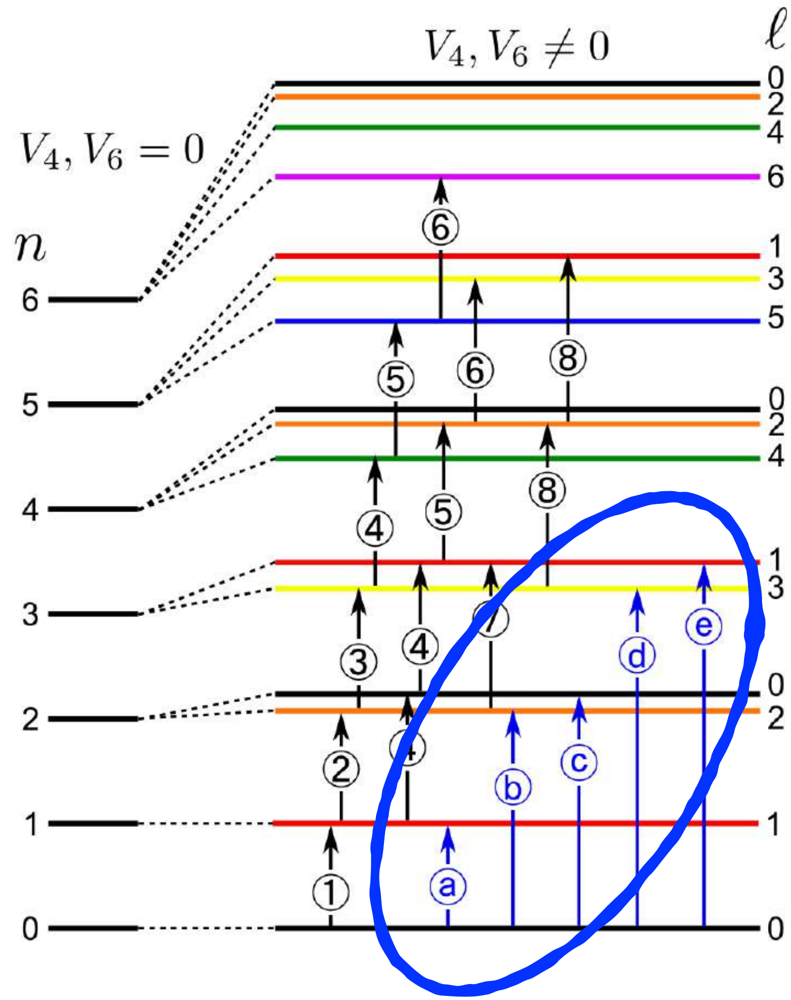


Rõõm et al. Tallinn

Bacanu et al. JCP (2021)

Inelastic neutron scattering

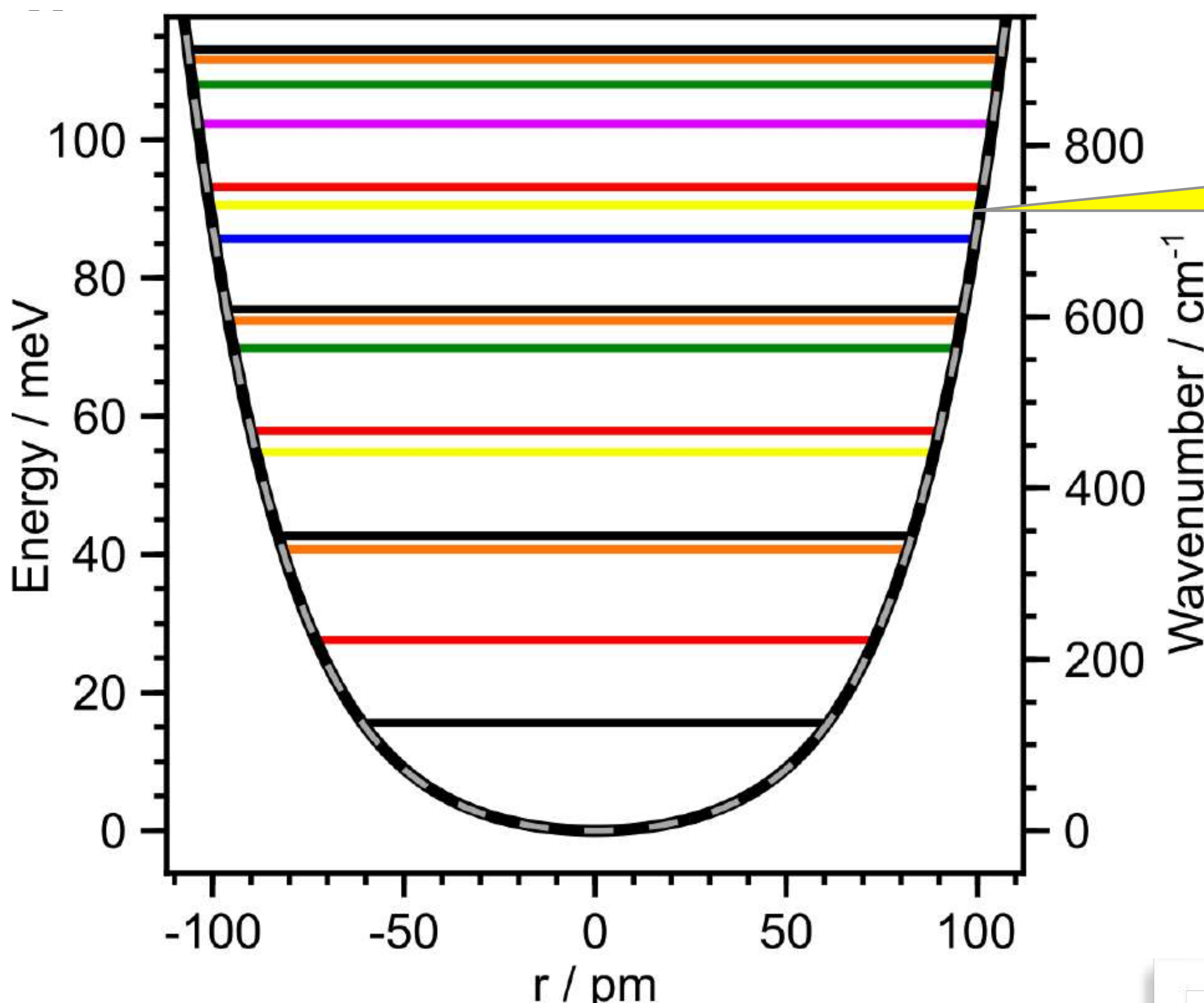




Rols et al. ILL-Grenoble

Bacanu et al. JCP (2021)

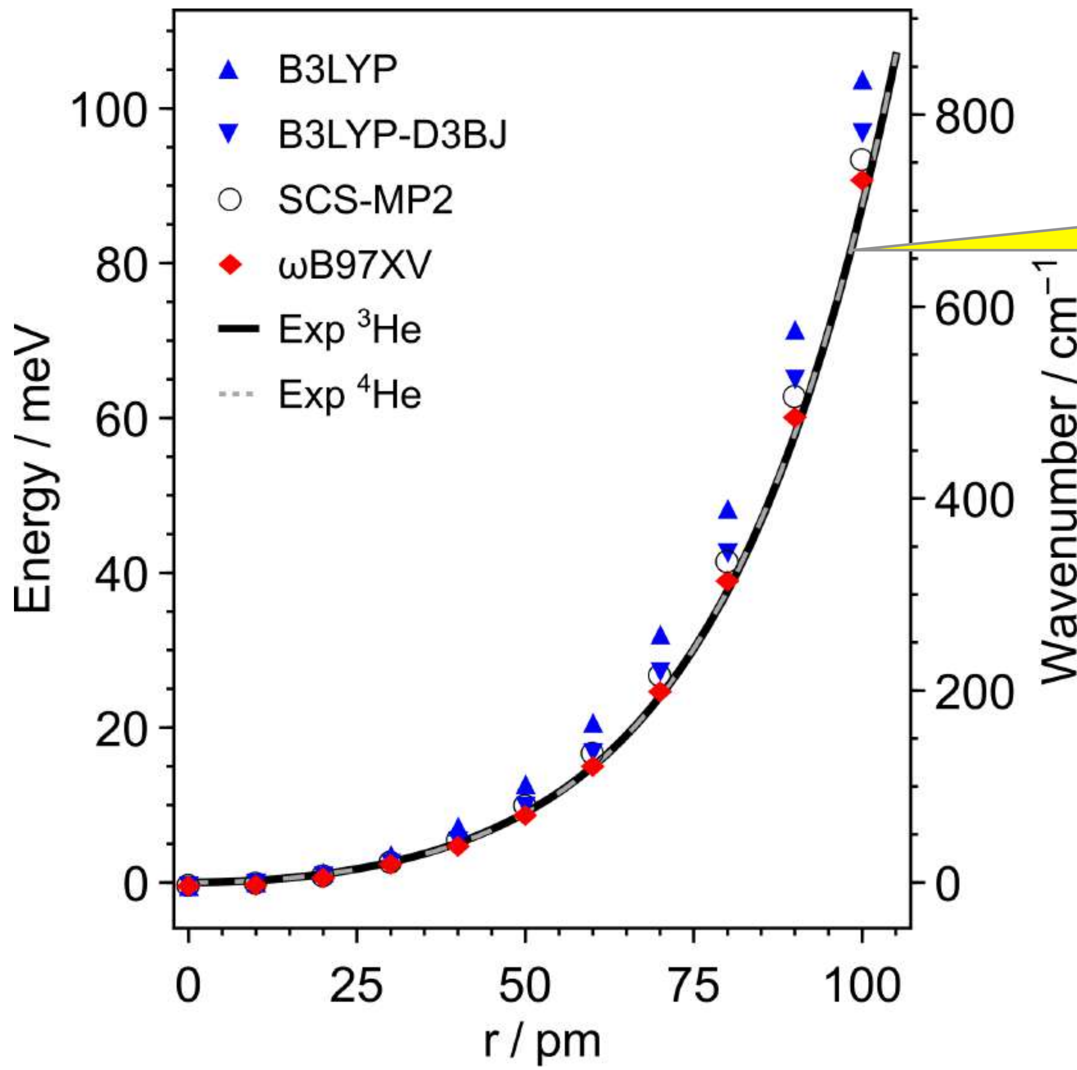
Experimentally determined $V(r)$ for $He@C_{60}$



³He and ⁴He curves (superimposed)

Bacanu et al. JCP (2021)

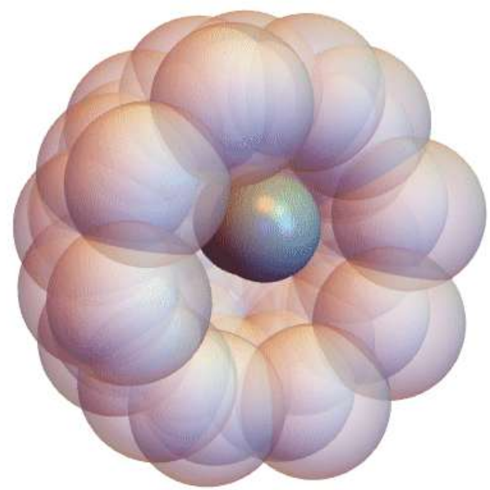
Comparison with QChem



^{3}He and ^{4}He curves (superimposed)

Bacanu et al. JCP (2021)

$H_2@C_{60}$



Spin isomers

Wolfgang Pauli

Pauli in 1945

Werner Heisenberg

Heisenberg in 1933

Spin-statistics theorem

the many-body wave function for elementary particles with integer spin (bosons) is symmetric under the exchange of any two particles, whereas for particles with half-integer spin (fermions), the wave function is antisymmetric under such an exchange.

Wolfgang Pauli

Pauli in 1945

Spin isomers of H_2

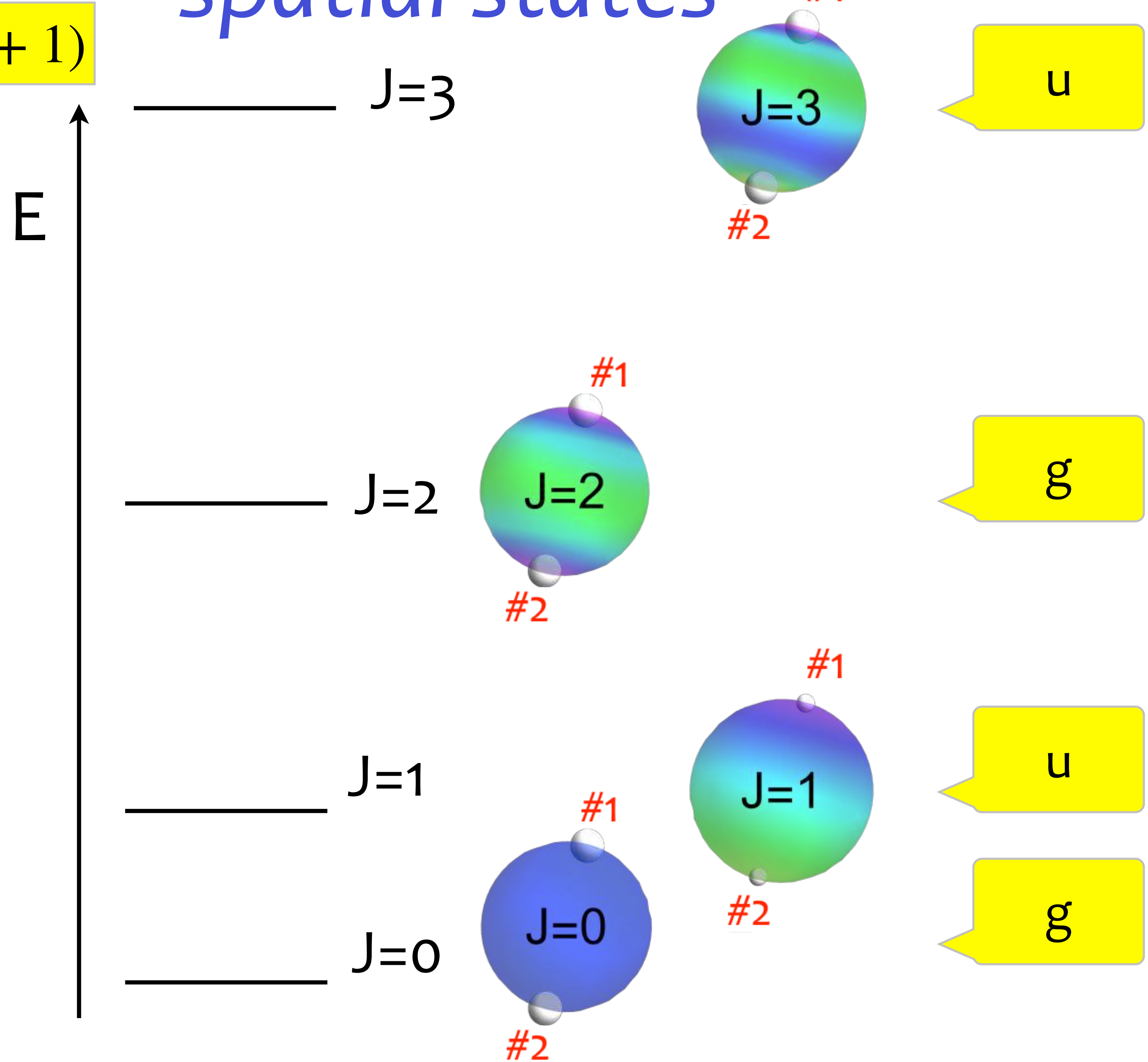
- H nuclei are fermions ($I = \frac{1}{2}$)
- quantum state must be antisymmetric ("ungerade", *u*) with respect to exchange:

$$(12)\Psi_{1,2}(12)^{\dagger} = -\,\Psi_{1,2}(12)$$

- The allowed spatial-spin combinations are *gu* and *ug*

spatial states

$$E_J = BJ(J+1)$$



H_2 nuclear spin states

- g symmetry:

$$|\alpha\alpha>$$

$$2^{-1/2}(|\alpha\beta> + |\beta\alpha>)$$

$$|\beta\beta>$$

$I = 1$

nuclear spin triplet

- u symmetry:

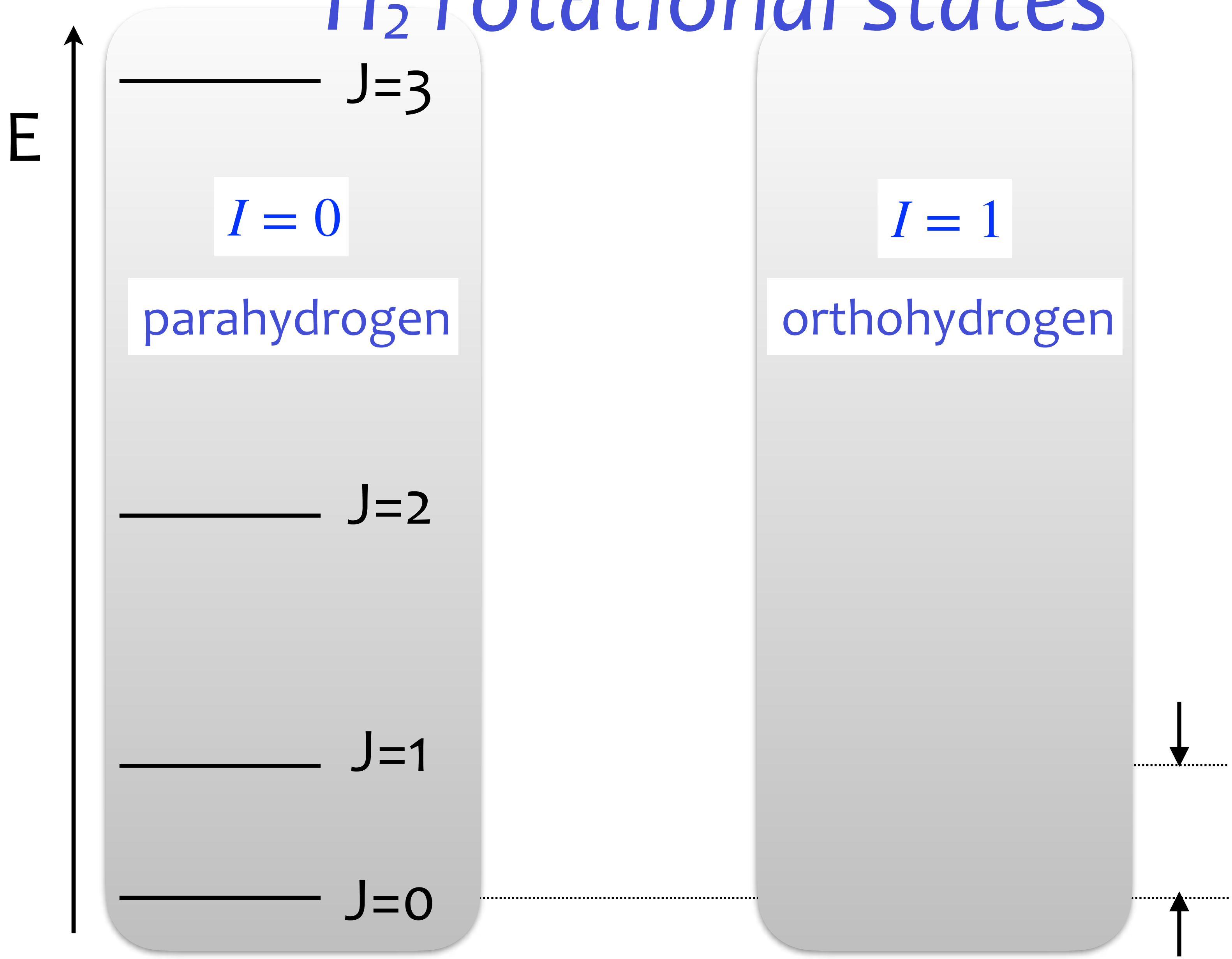
$$2^{-1/2}(|\alpha\beta> - |\beta\alpha>)$$

$I = 0$

nuclear spin singlet

H_2 spin isomers

H_2 rotational states



Heisenberg in 1933

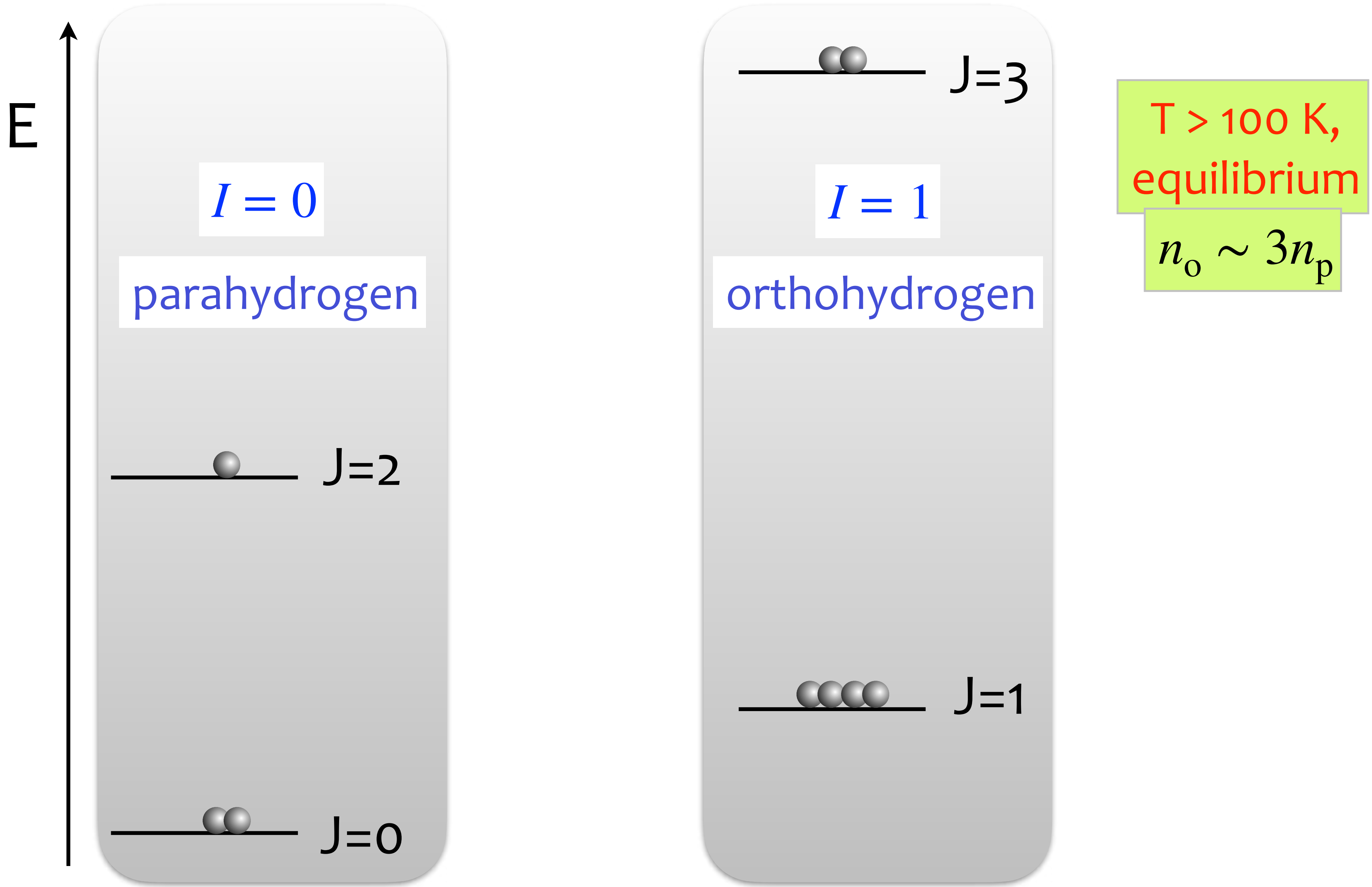
15.1 meV

174 K

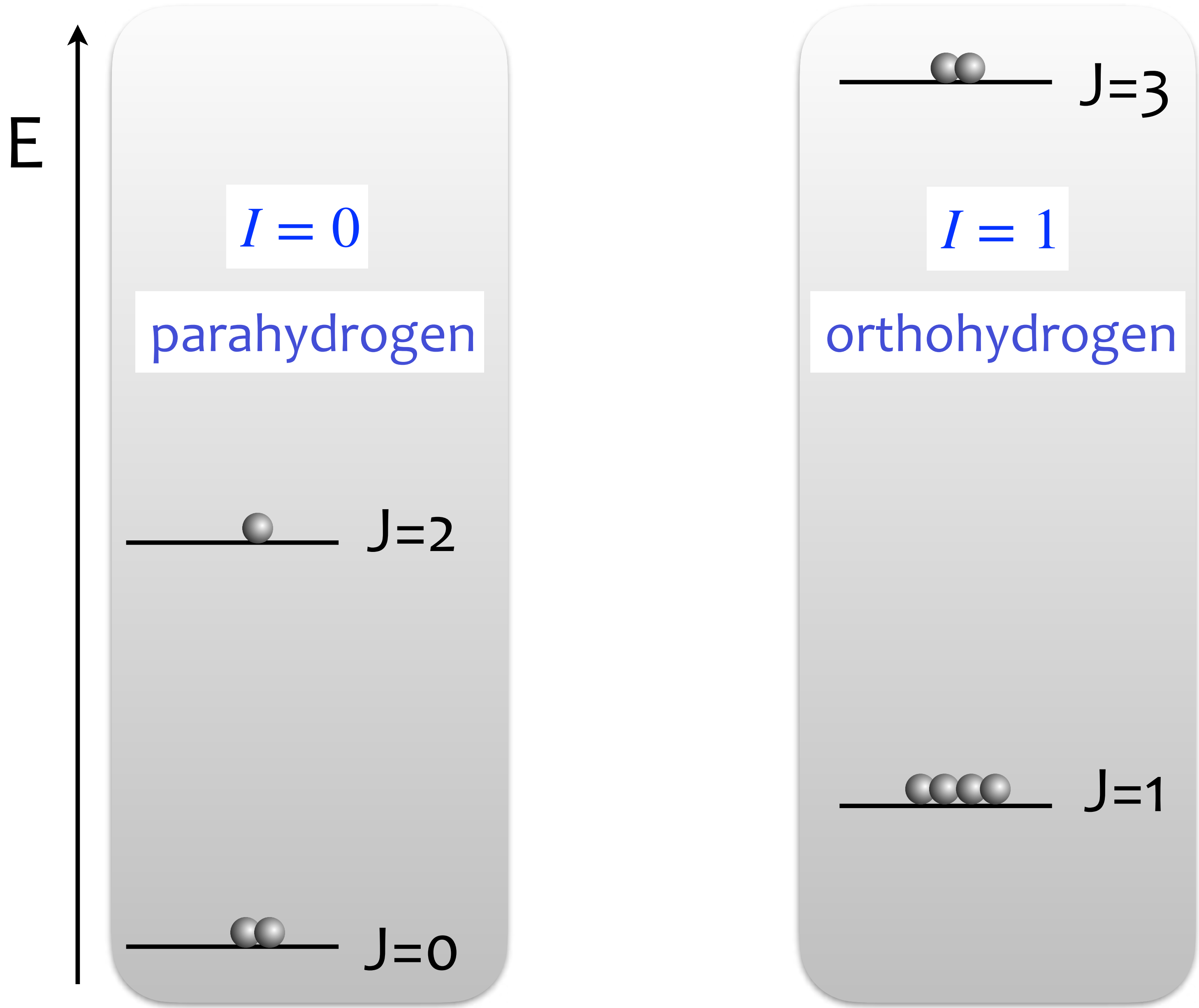
121.6 cm^{-1}

3.6 THz

high temperature



low temperature
high temperature



T > 100 K, equilibrium

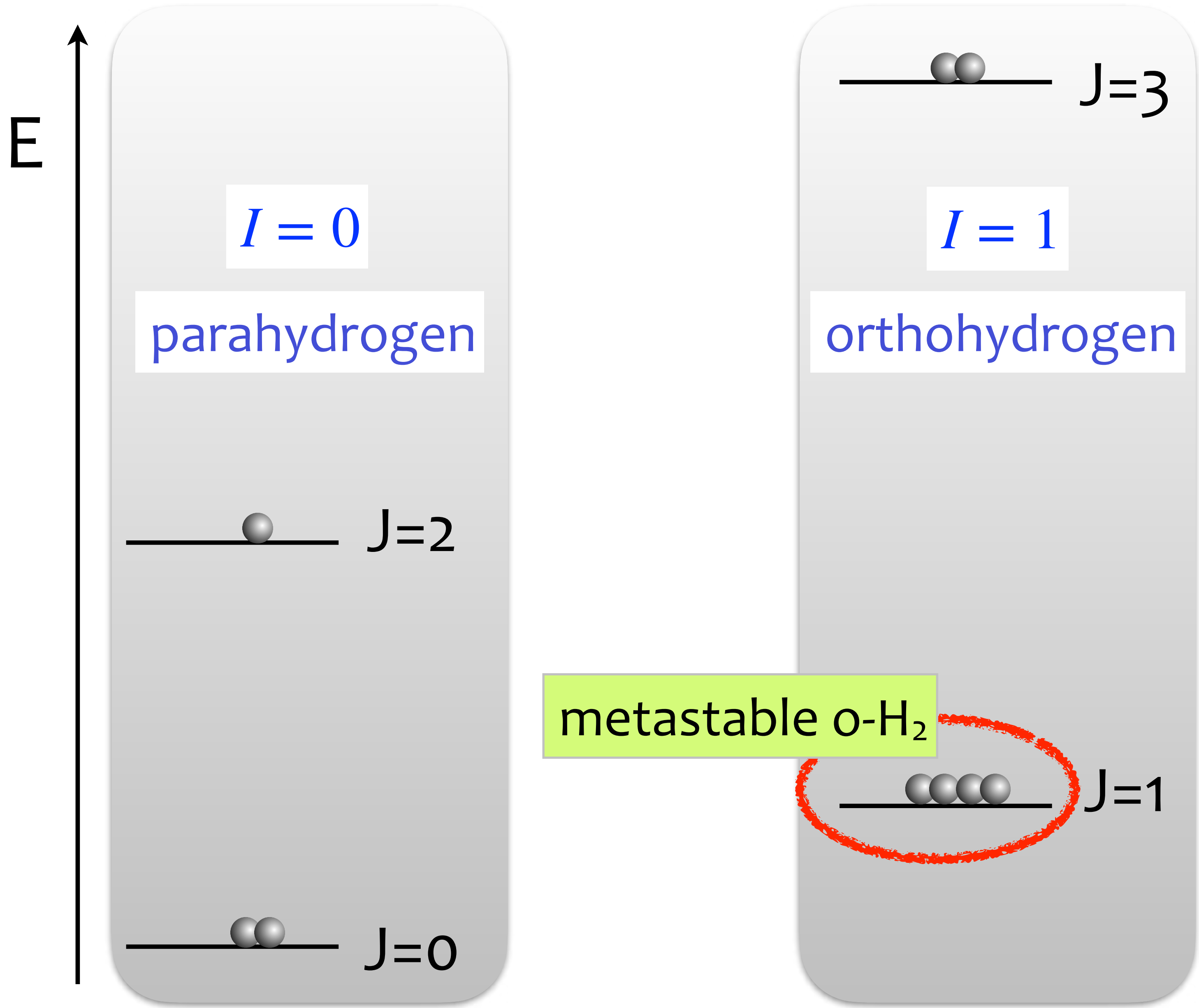
$n_o \sim 3n_p$

T < 20 K, equilibrium

$n_o \sim 0$

high temperature

low temperature



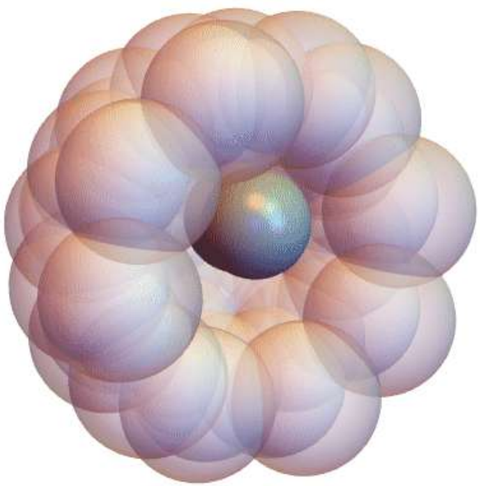
T > 100 K, equilibrium

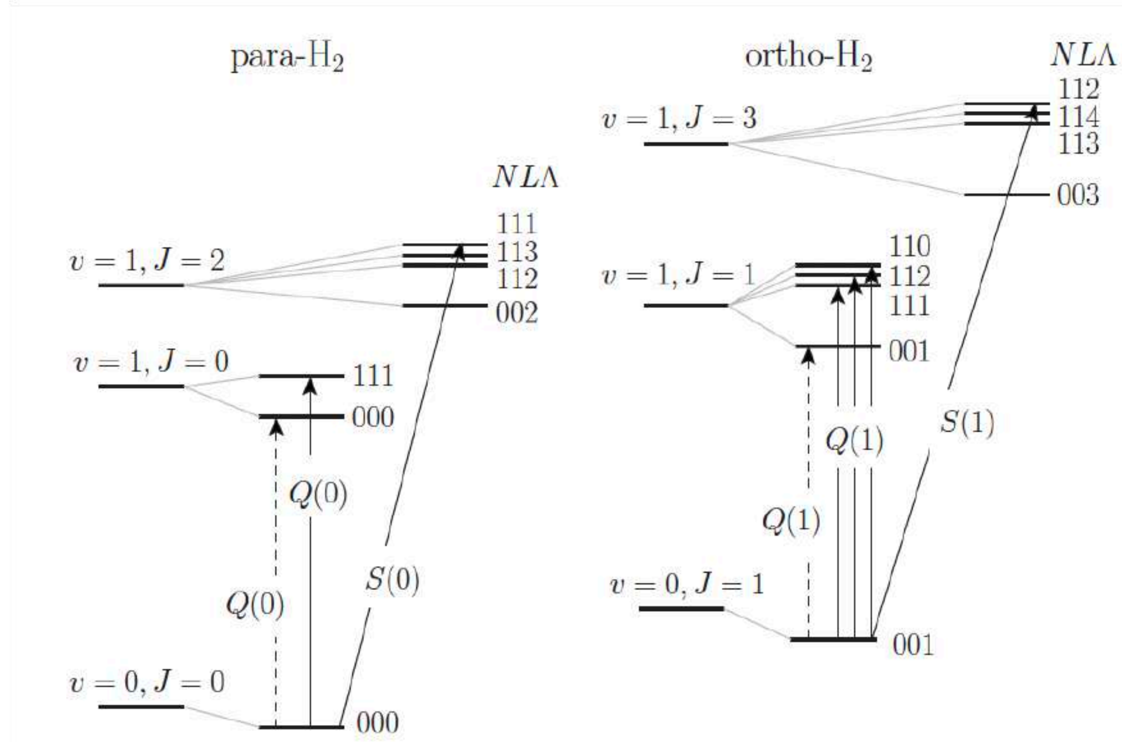
$n_o \sim 3n_p$

T < 20 K, quasi-equilibrium

$n_o \sim 3n_p$

Rotational-translational states





THE JOURNAL OF CHEMICAL PHYSICS **130**, 081103 (2009)

Rotor in a cage: Infrared spectroscopy of an endohedral hydrogen-fullerene complex

S. Mamone,[1] Min Ge,[2] D. Hüvonen,[2] U. Nagel,[2] A. Danquigny,[1] F. Cuda,[1] M. C. Grossel,[1] Y. Murata,[3] K. Komatsu,[3] M. H. Levitt,[1] T. Rõõm,[2] and M. Carravetta[1,a)]

Inelastic neutron scattering

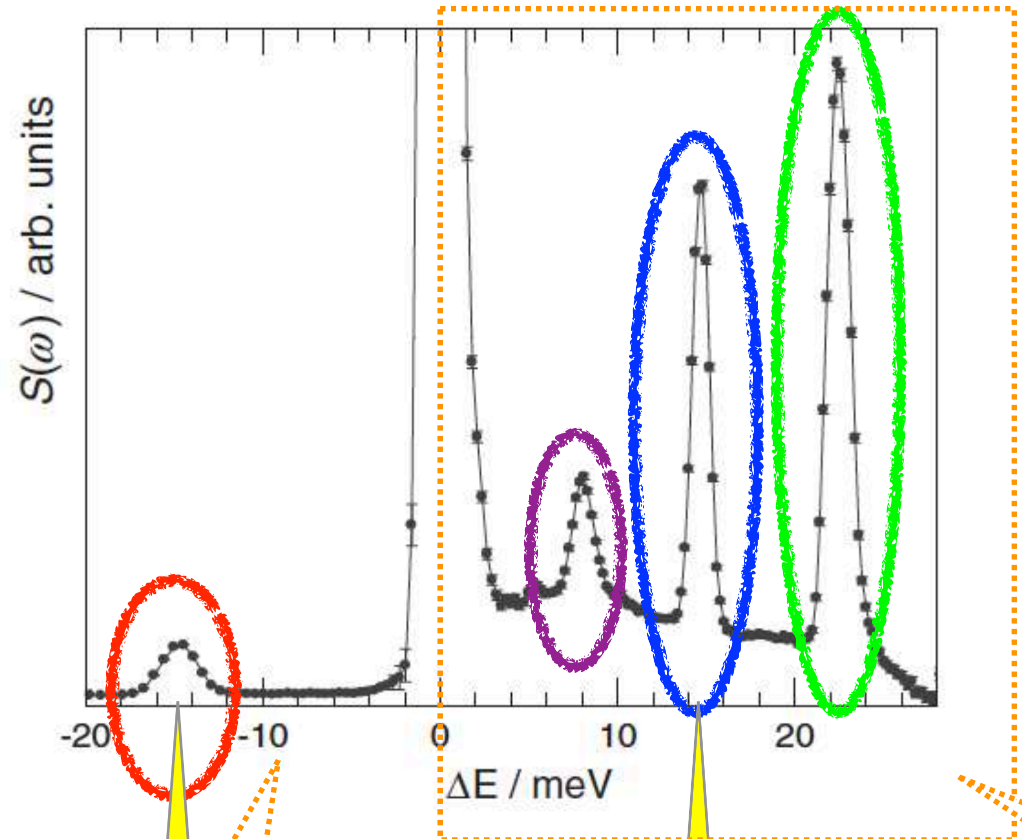
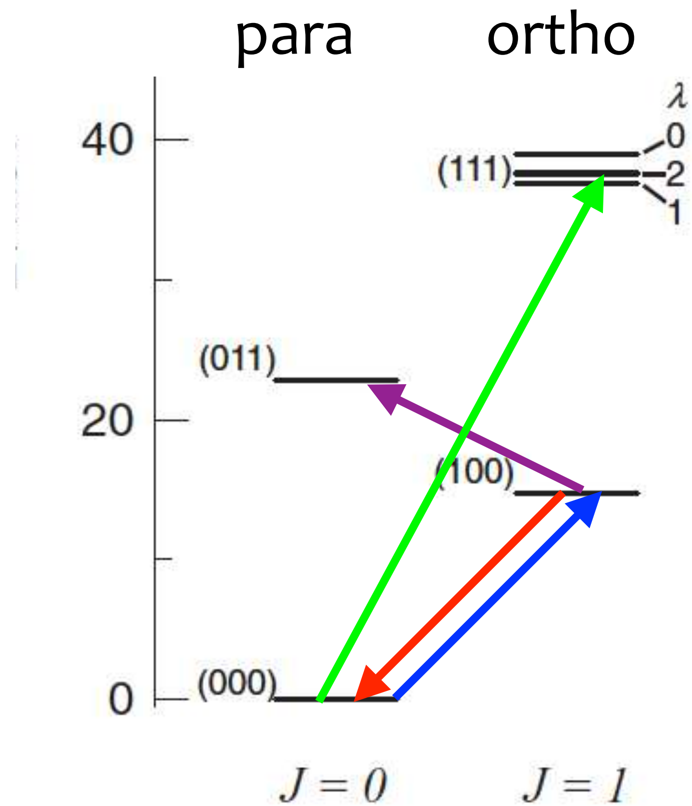


FIG. 3. The I... pectrum of $H_2@C_{60}$ reco...led on IN4C at 1.6 K.



neutron energy gain

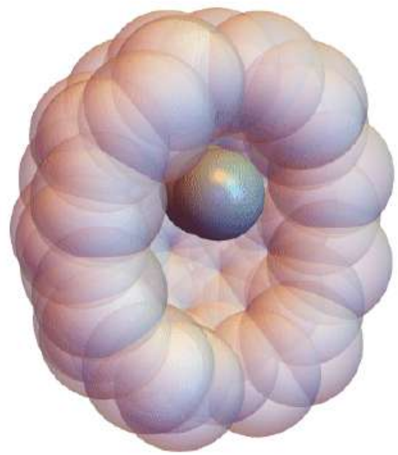
...meV

+14.6 meV

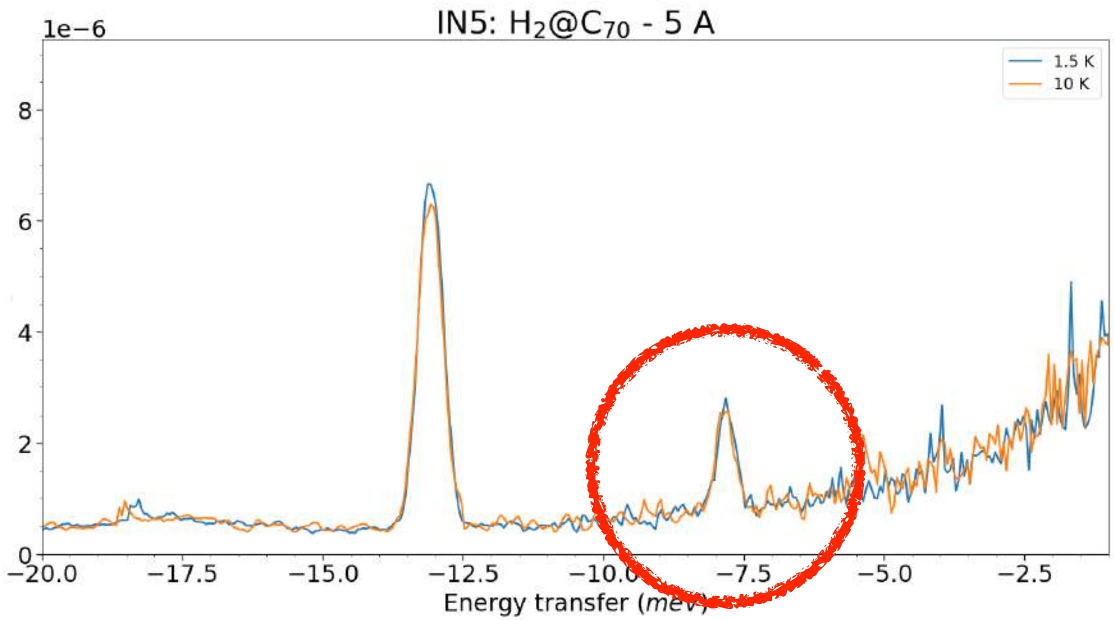
neutron energy loss

NYU-A

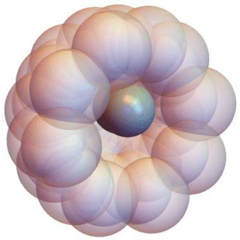
$H_2@C_{70}$



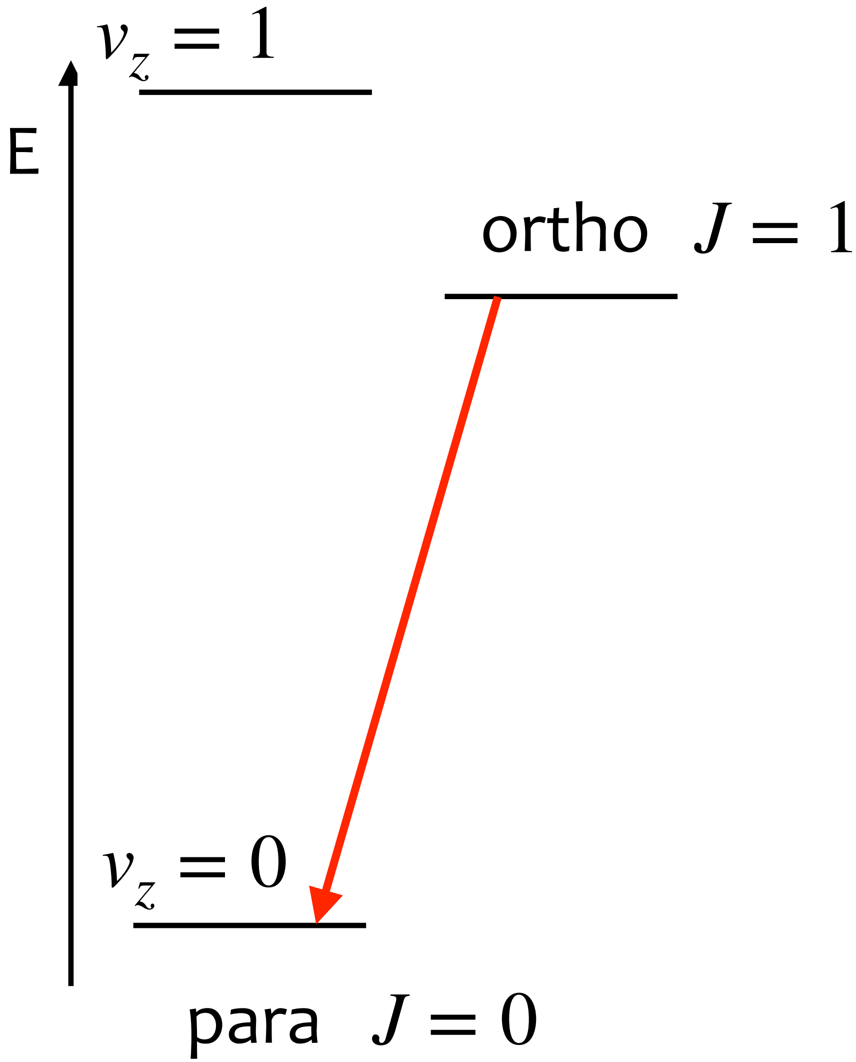
NE gain

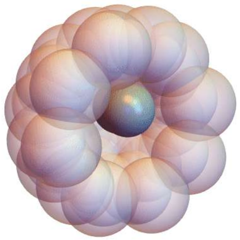


Second NEG peak

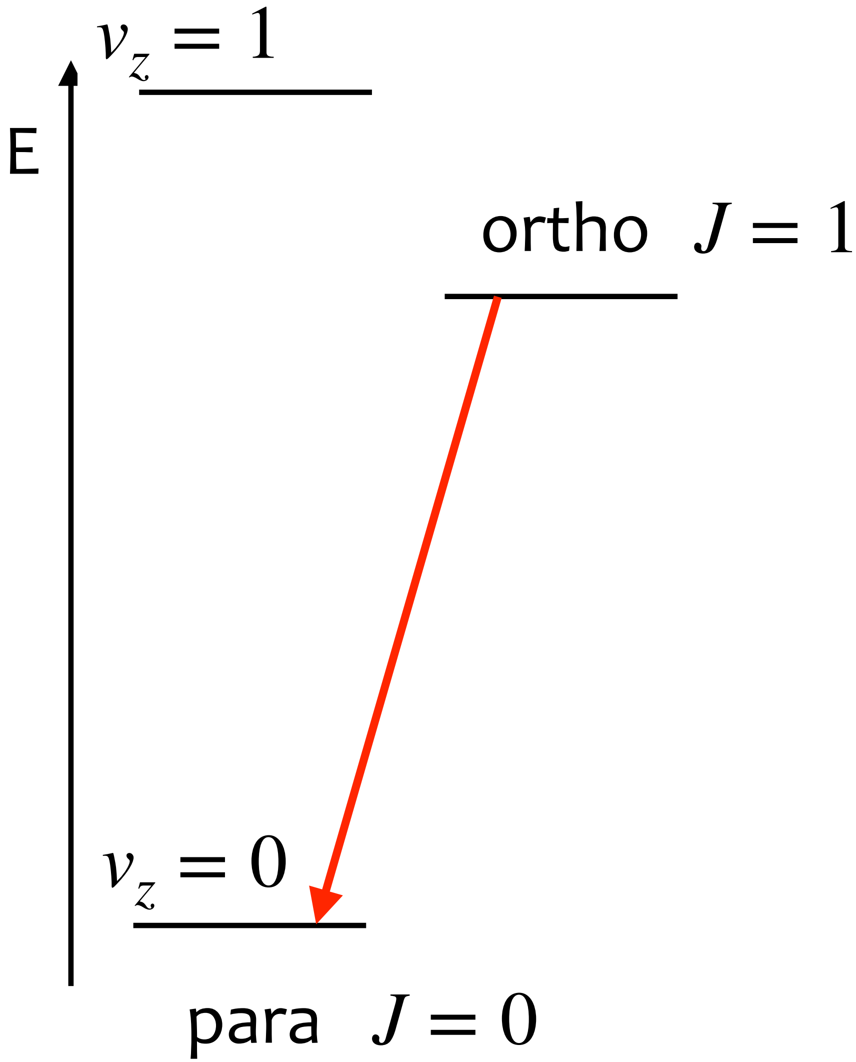


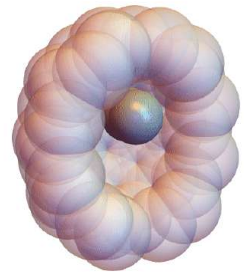
$H_2@C_{60}$



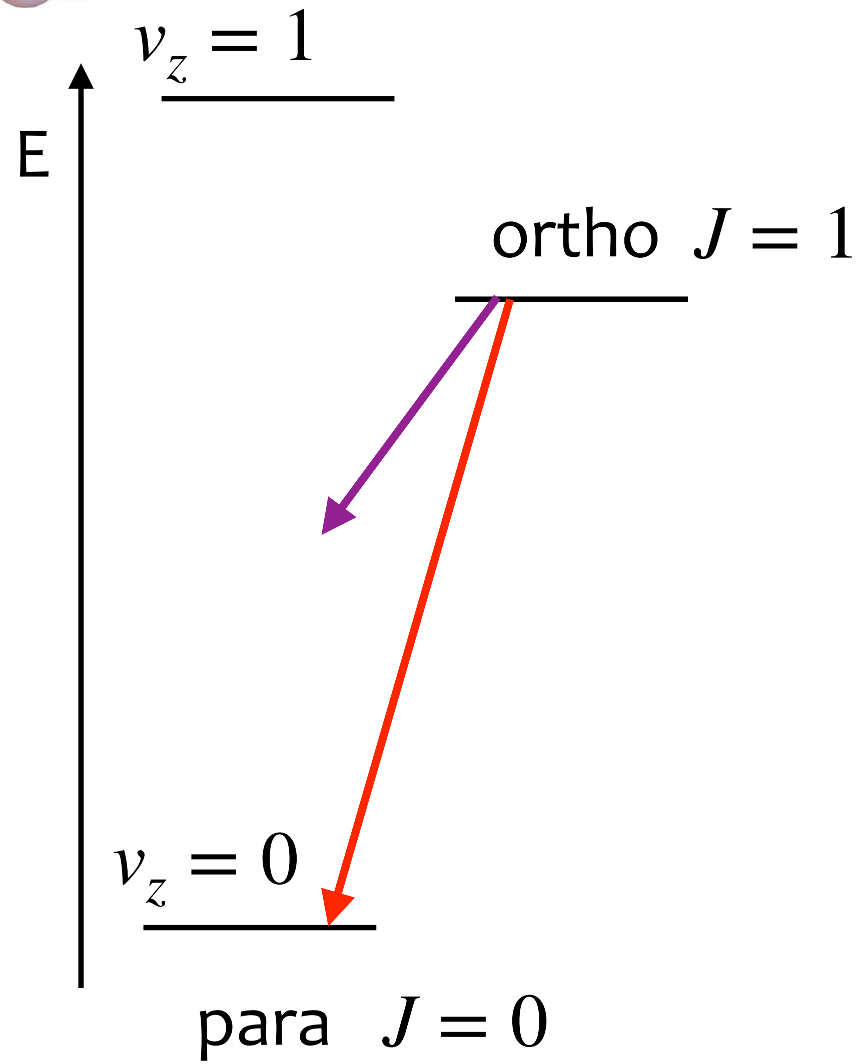


$H_2@C_{60}$

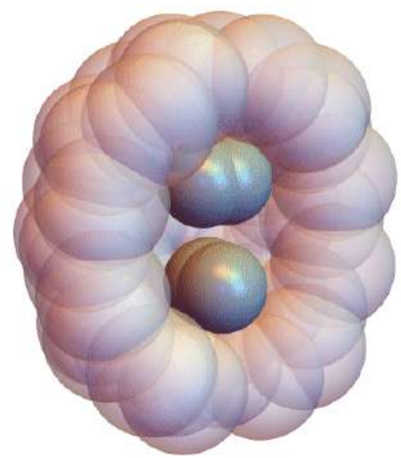




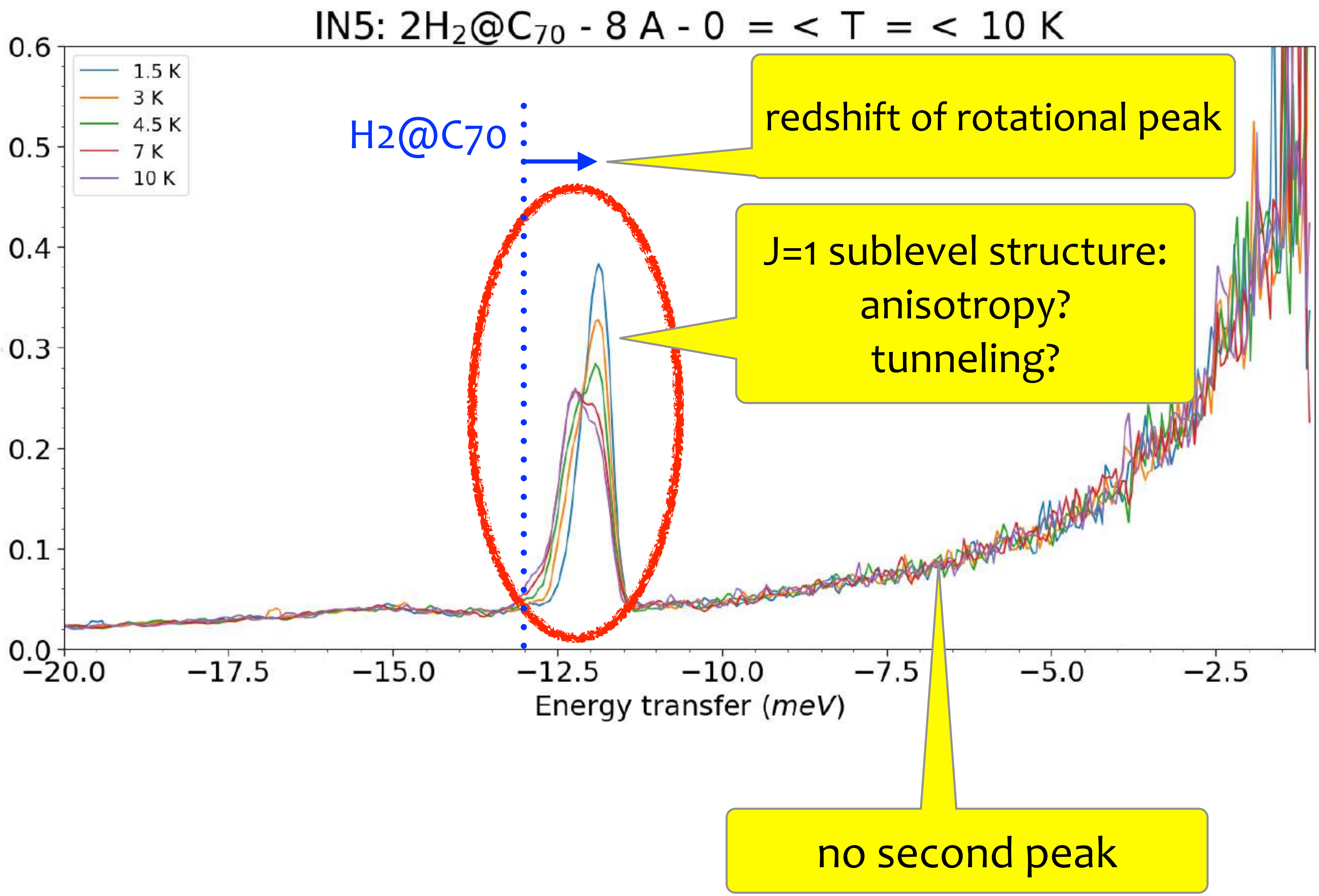
$H_2@C_{70}$



$2H_2@C_{70}$

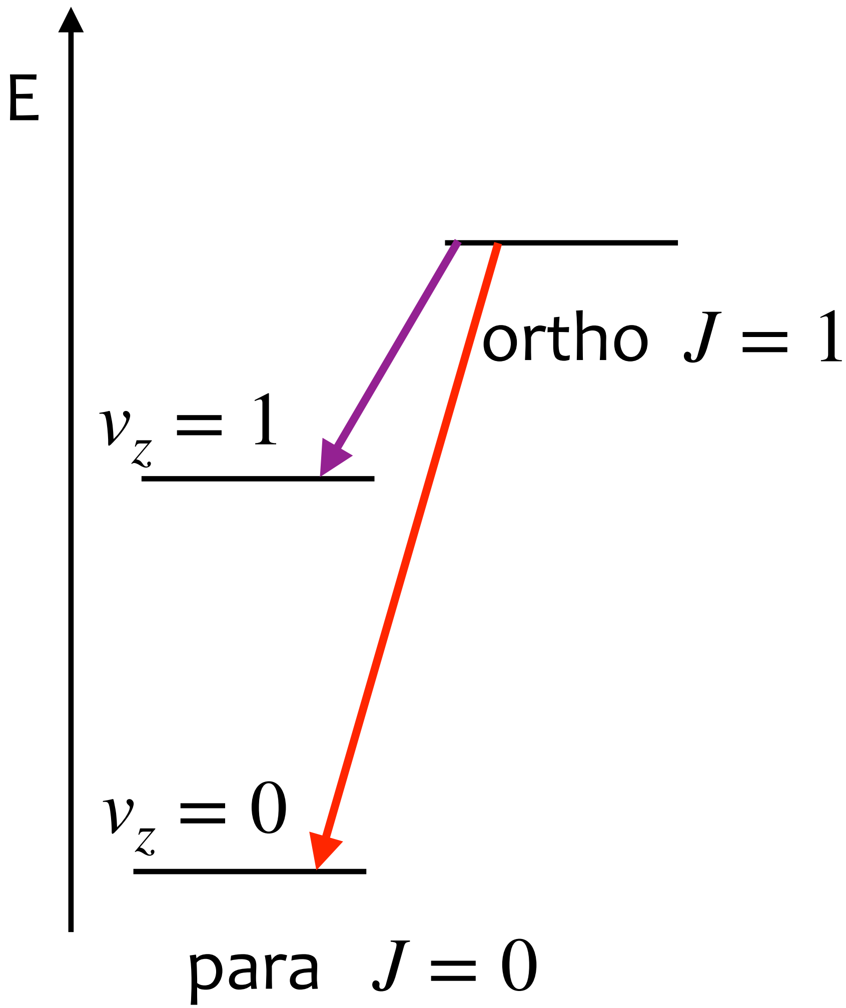


NE gain

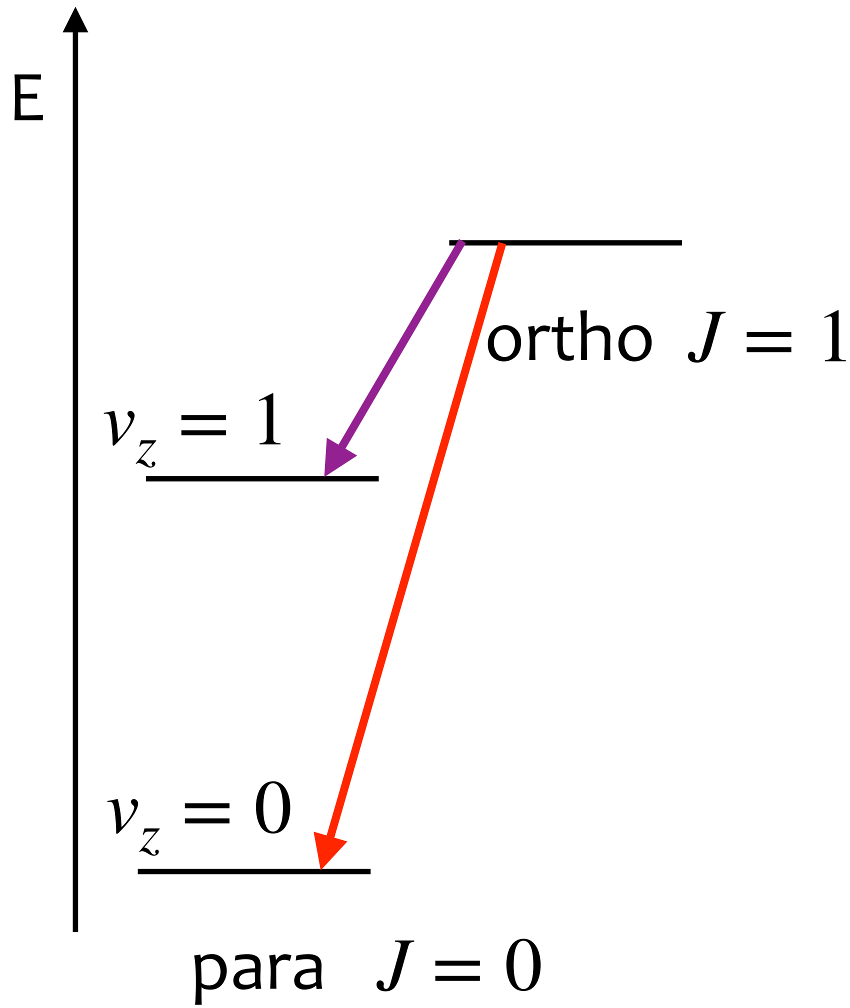


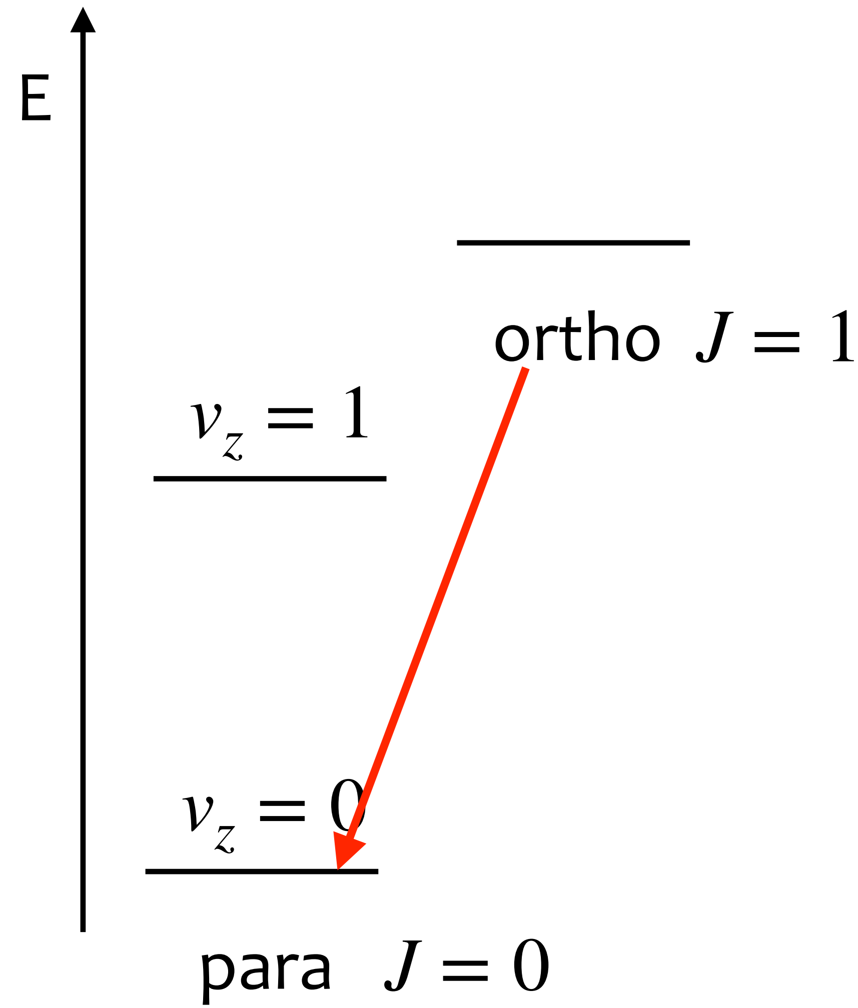
IN5: $2H_2@C_{70}$ - 8 A - 0 = < T = < 10 K
1.5 K
3 K
4.5 K
7 K
10 K
H2@C70
redshift of rotational peak
J=1 sublevel structure:
anisotropy?
tunneling?
no second peak
Energy transfer (meV)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
−20.0
−17.5
−15.0
−12.5
−10.0
−7.5
−5.0
−2.5

$H_2@C_{70}$



$H_2@C_{70}$ and 2H2@C70

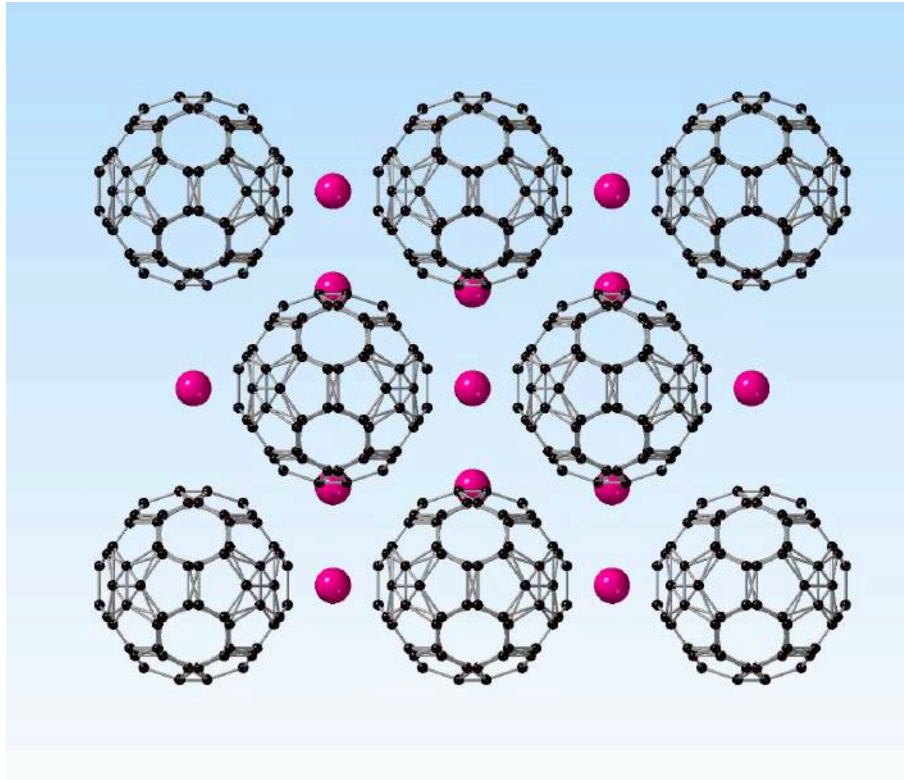




$2H_2@C_{70}$

- Changes with respect to $H_2@C_{70}$:
  - rotational splitting much smaller
    - increased effective moment of inertia?
  - absence of translational NEG peak
    - translational splitting > rotational energy
    - each H_2 has less room
  - structure in ortho (and para?) ground state
    - rotational anisotropy?
    - tunneling splitting?

Rb_3C_{60}



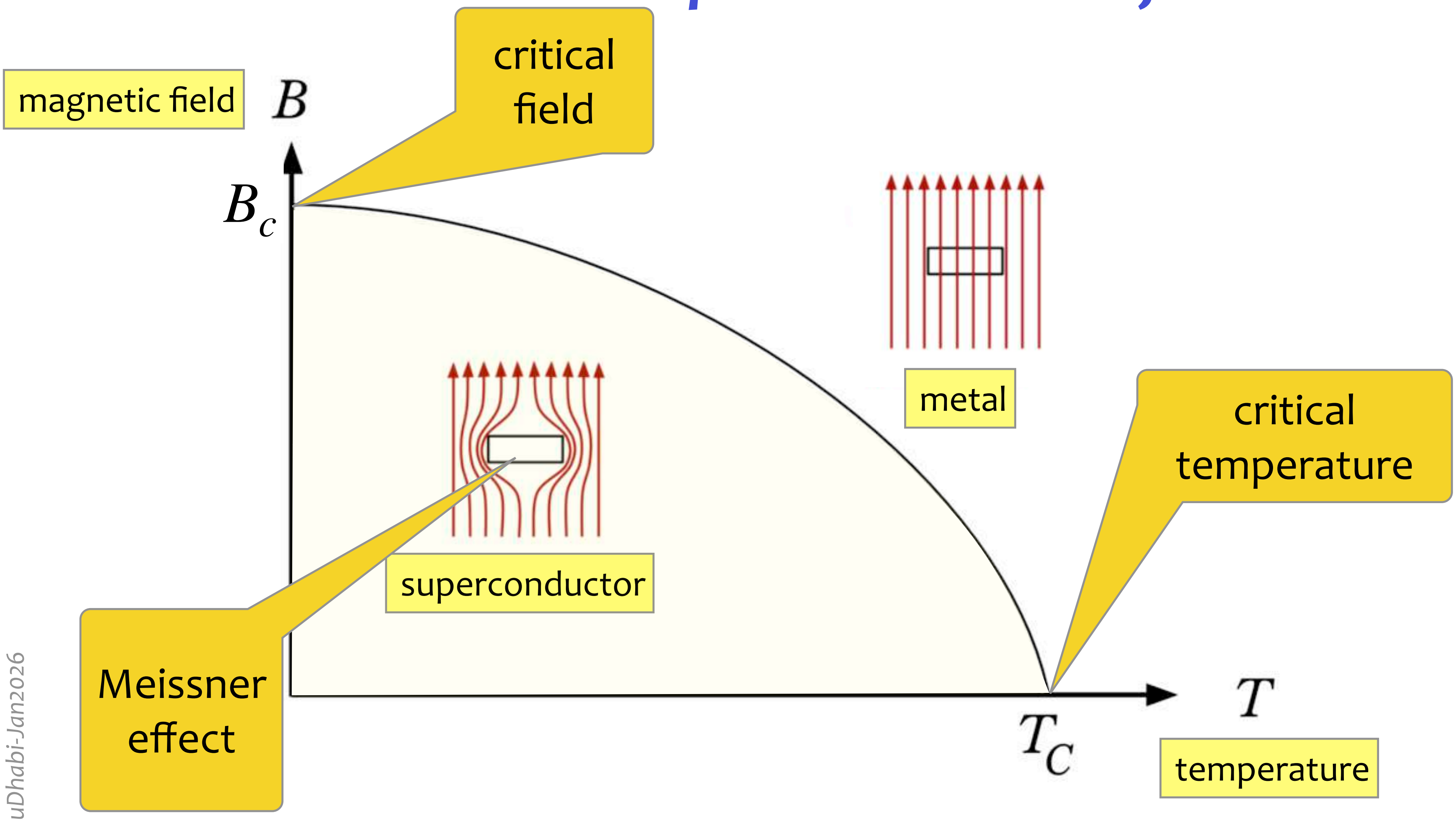
$T_c \simeq 30.3\,\mathrm{K}$

VOLUME 66, NUMBER 21 PHYSICAL REVIEW LETTERS 27 MAY 1991

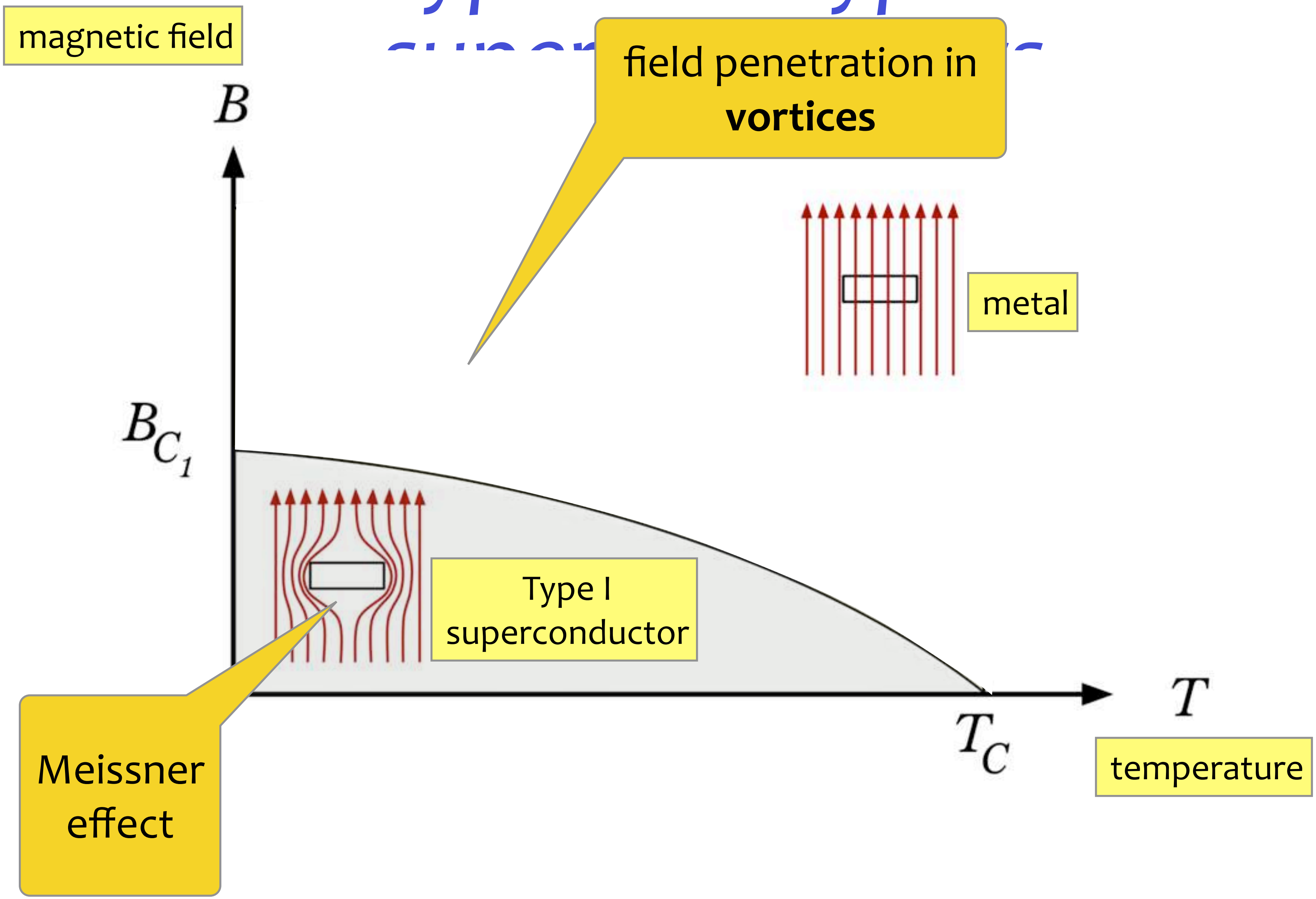
Superconductivity at 28 K in Rb_xC_{60}

M. J. Rosseinsky, A. P. Ramirez, S. H. Glarum, D. W. Murphy, R. C. Haddon, A. F. Hebard,
T. T. M. Palstra, A. R. Kortan, S. M. Zahurak, and A. V. Makhija

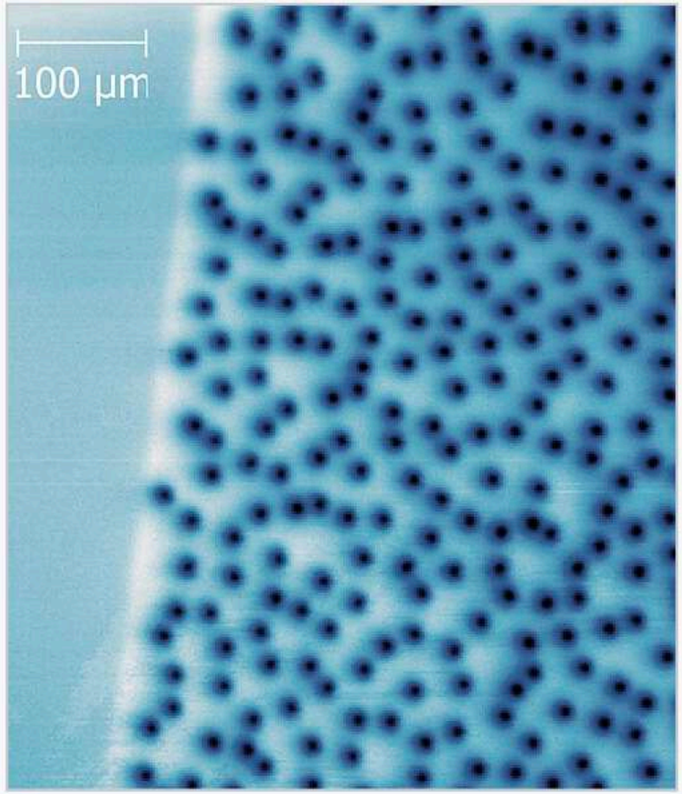
critical temperature & field



type I and type II

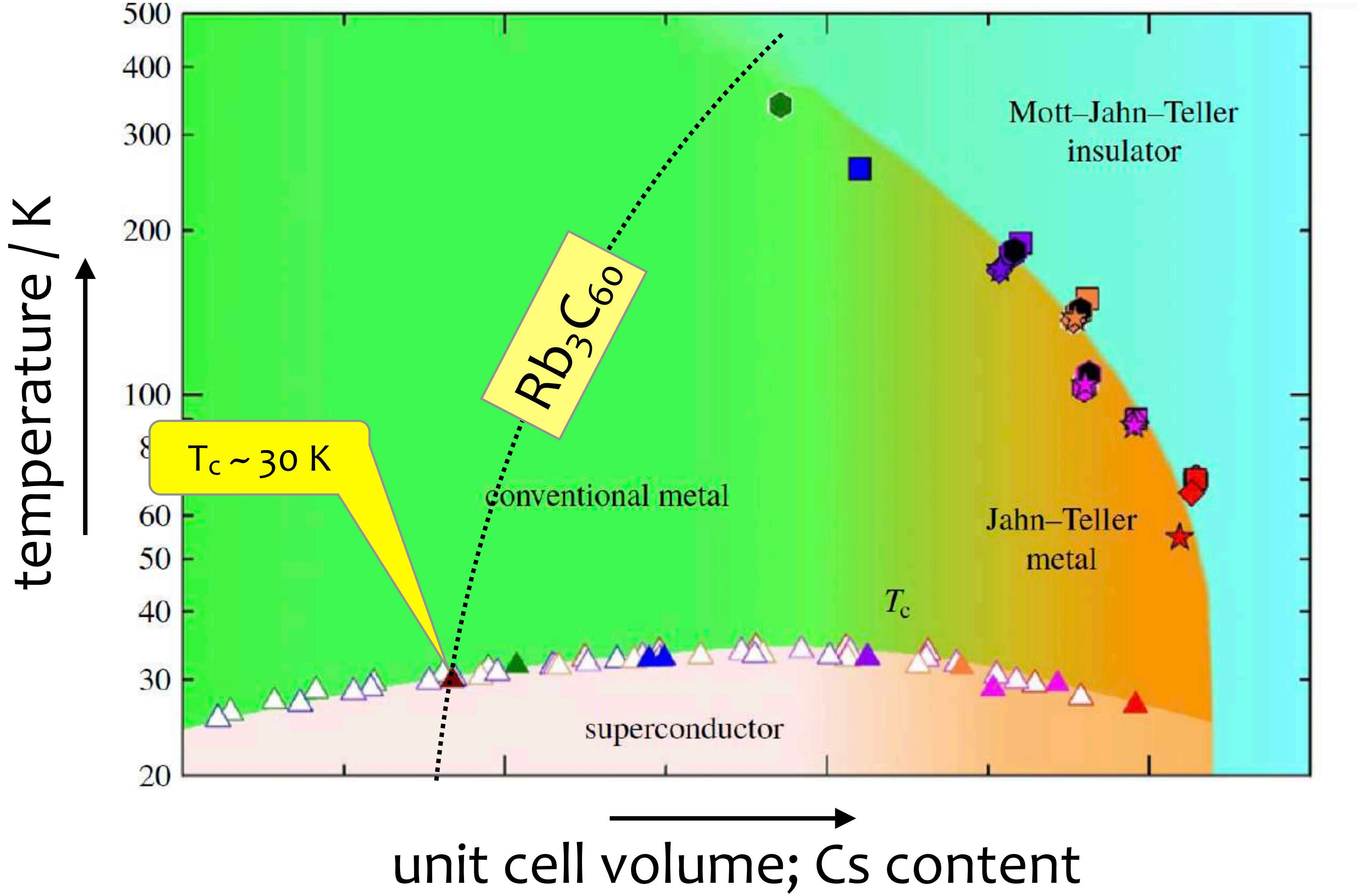


vortices



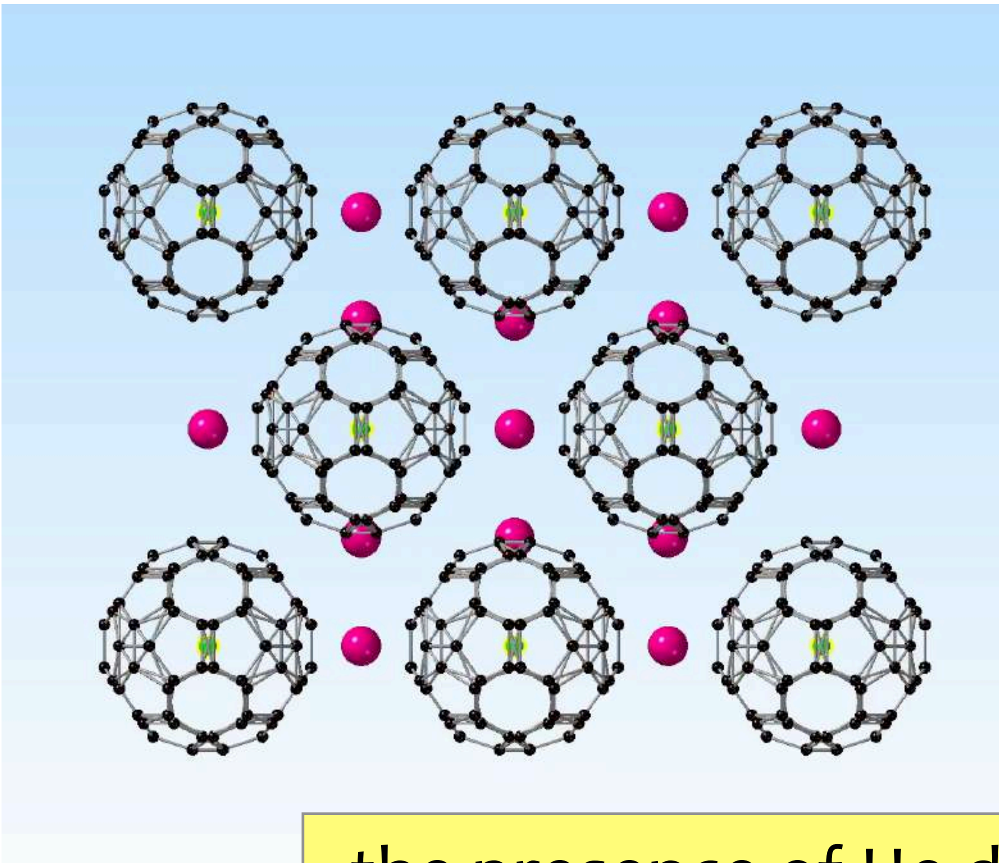
Quantum vortices in a 200-nm-thick YBCO film imaged by scanning SQUID microscopy[1]

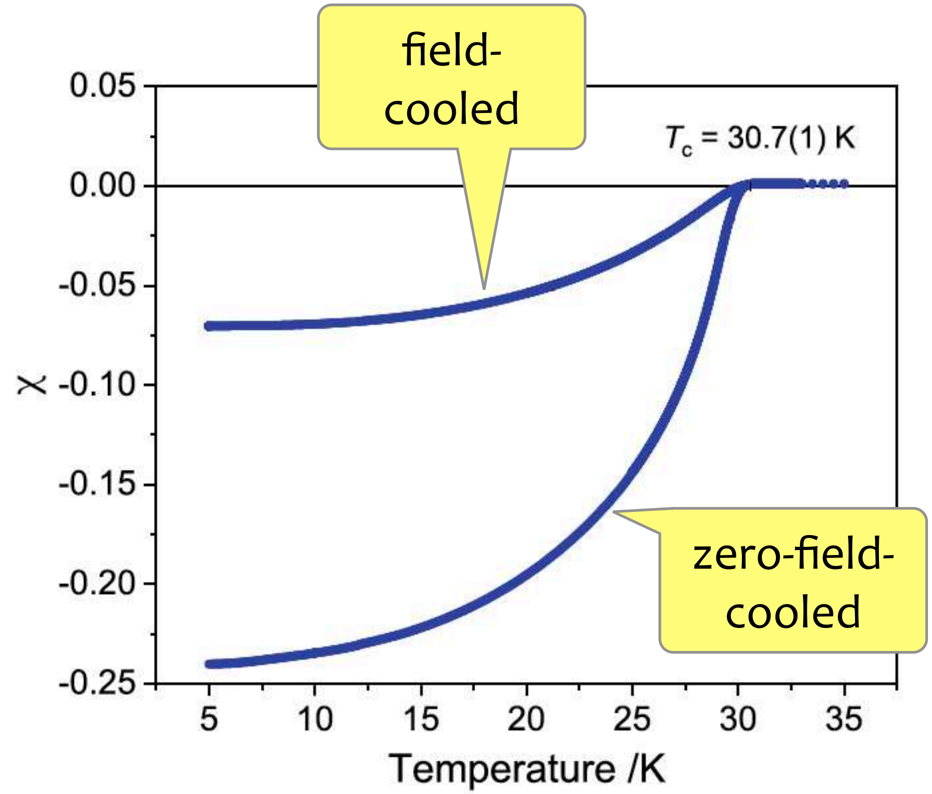
$Rb_x Cs_{3-x} C_{60}$



temperature / K
500
400
300
200
100
60
50
40
30
20
Mott–Jahn–Teller insulator
Rb_3C_{60}
T_c ~ 30 K
conventional metal
Jahn–Teller metal
T_c
superconductor
unit cell volume; Cs content

$Rb_3(^3He@C_{60})$



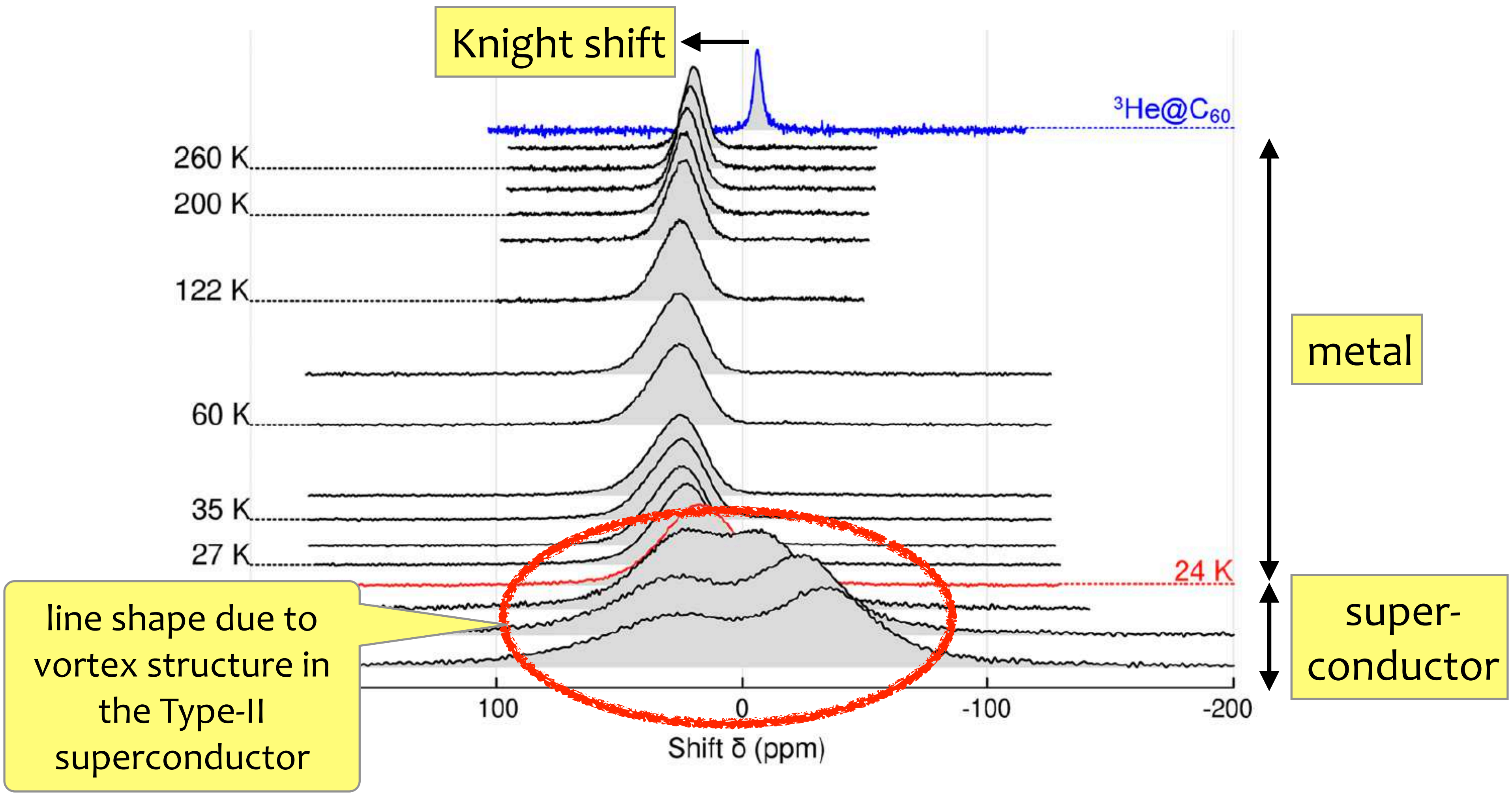


the presence of He does not change the superconductivity

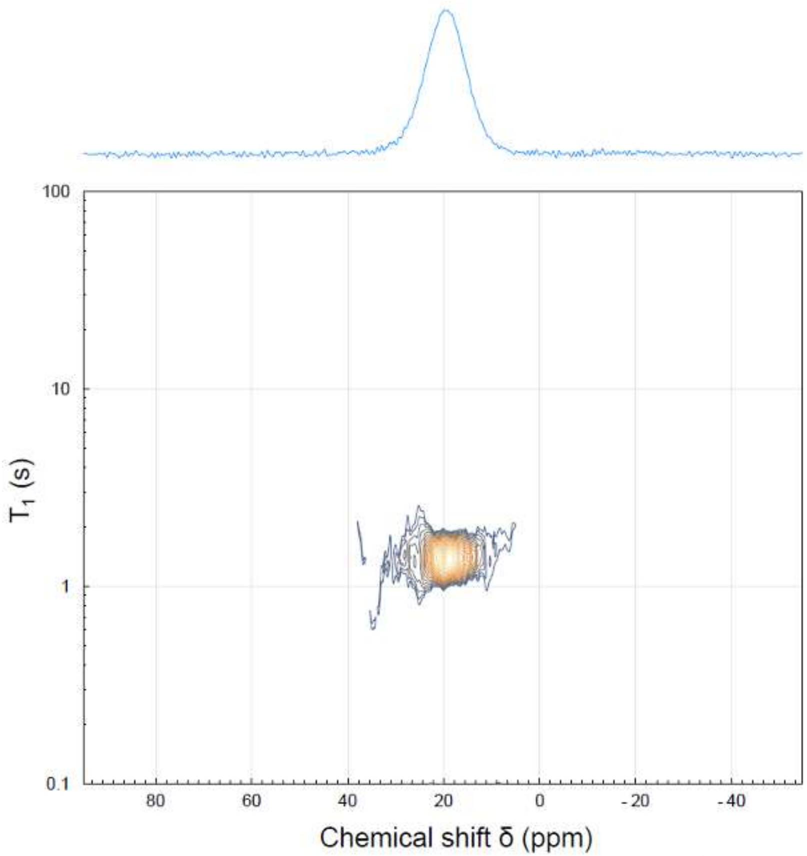
Solid-state ^{3}He NMR

- ^{3}He is an excellent NMR nucleus
  - spin-1/2
  - high-γ (3/4 that of ^{1}H)
- very narrow NMR line
- zero background
- negligible anisotropic interactions

solid-state ^{3}He NMR of $Rb_3(^3He@C_{60})$

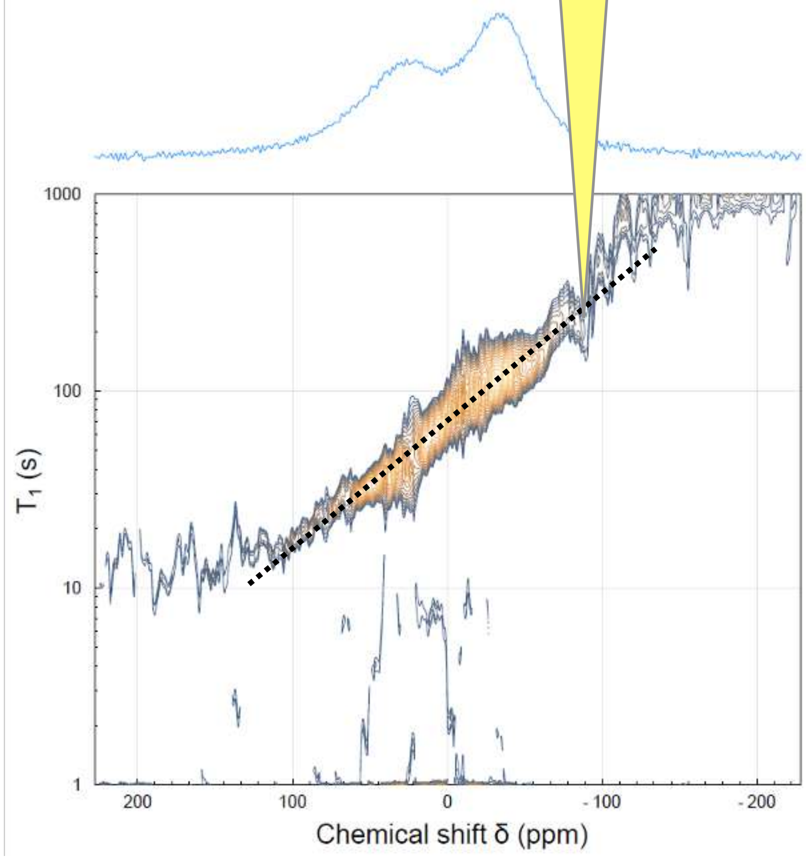


^{3}He T_1 versus δ



290 K

normal metal



15 K

superconductor

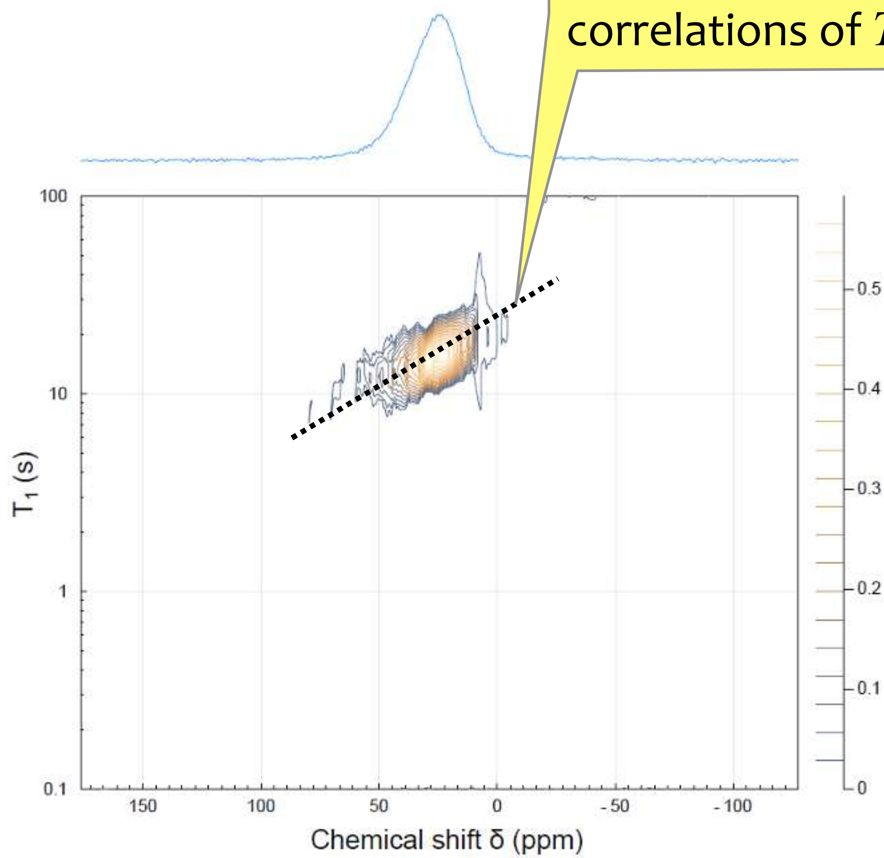
correlation of T_1 with δ

Inverse Laplace transform in the "T_1 dimension"

^{3}He T_1 versus δ

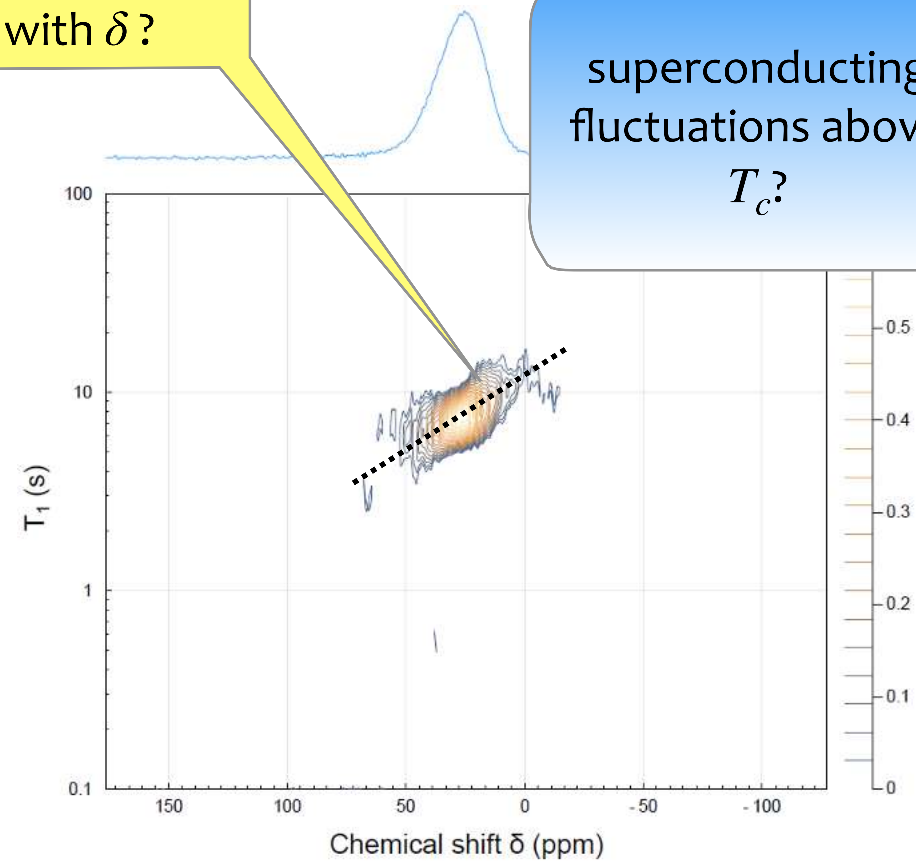
correlations of T_1 with δ ?

superconducting fluctuations above T_c?



30 K

normal metal, just above T_c



60 K

normal metal, 30 K above T_c

Summary

- Endofullerenes provide confined molecules and atoms in a homogeneous chemical environment, in macroscopic quantities
- Confinement leads to translational quantisation
- THz and INS allows determination of intermolecular potentials
- non-bonded NMR J-couplings are observed
- The endo species is a sensitive NMR probe of electronic and molecular structure, even into the superconducting state

SYNTHESIS

Southampton

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  - Gabi Hoffman
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  - Francesco Giustiniano
  - Vijyesh Vyas

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NMR, theory

Southampton

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IR & THz, theory

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  - Tanzeeha Jafari
  - Urmas Nagel
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Neutron Scattering

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