

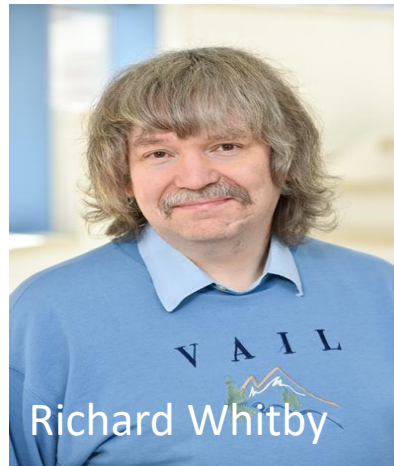
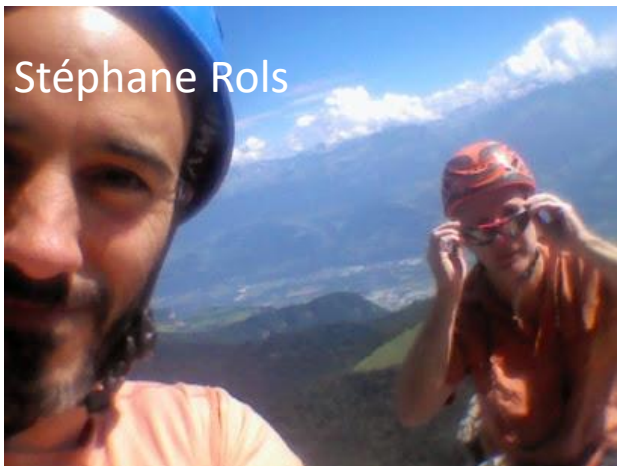
Inelastic Neutron Scattering of Endofullerenes

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CS Group - ILL

Hello!

Meet the team

PhD Supervisors:



Collaborators:

Mónica
Jimenez Ruiz

George
Bacanu

Spectro group

Outline

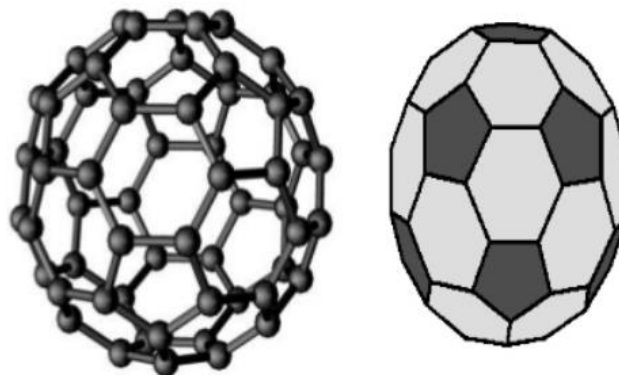
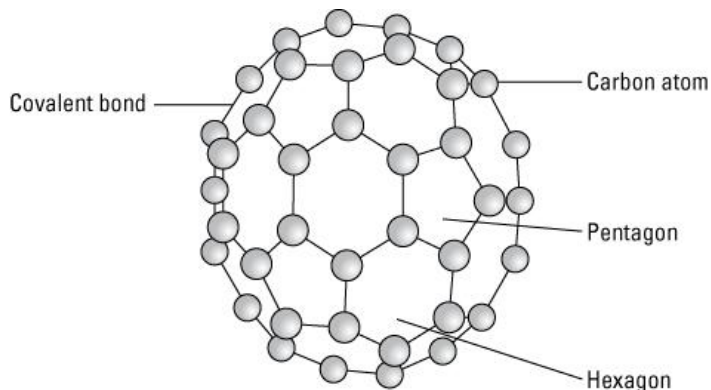
“What have I gotten myself into?” – Me, December 2019

- What’s a Fullerene?
- How about an Endofullerene?
 - What are they? How are they made? Why study them?
 - What’s new nowadays?
- DFT approach and theoretical models
- Experimental results.
- General remarks
- Future Work.

What's a Fullerene?

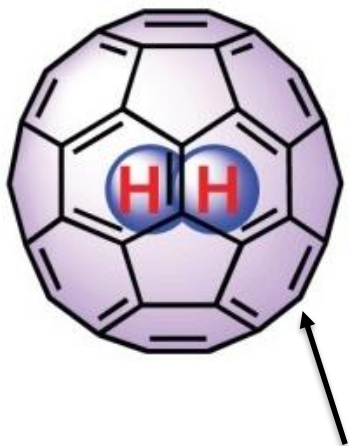
Let's set up some building blocks

- Yet another Carbon allotrope
- C_{60} is composed of 12 pentagons and 20 hexagons
- Gets the grand sum of 120 symmetry operations
- Very stable. Perfectly known properties (phase diagram, structure - dynamics...)



How about an endofullerene?

Endohedral Fullerenes! What's so special about them?



C_{60} = Nano-laboratory!

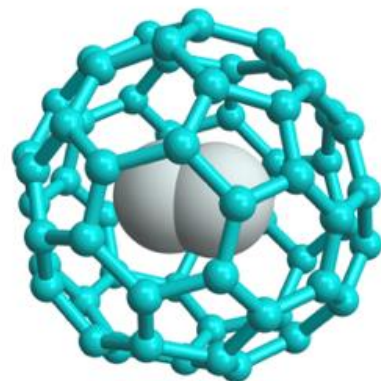
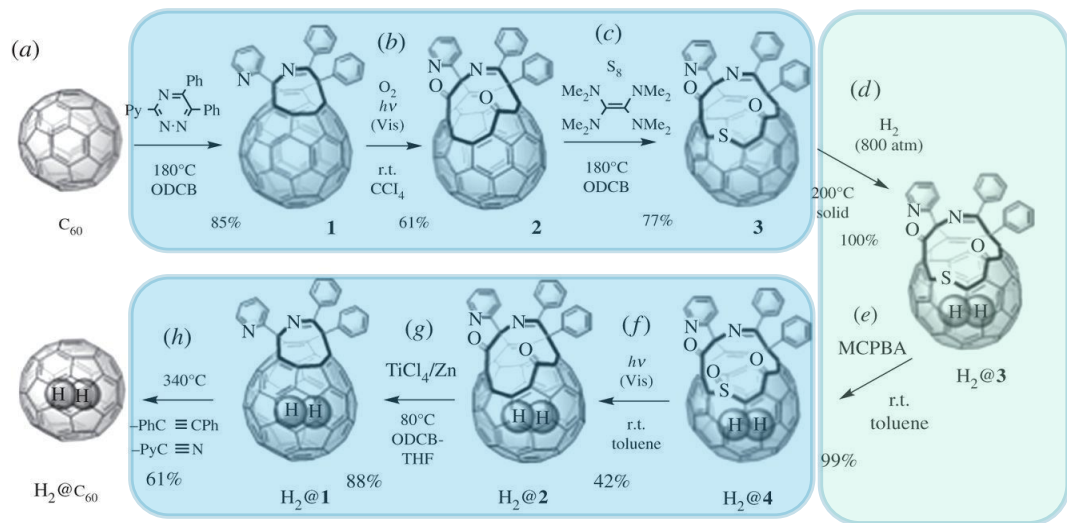
- Mostly fundamental interest « particle in a box »
- Make use of the high symmetry of C_{60}
- Trapped atom/molecule is perfectly confined in 3D
- Perfect for the study of quantum states of isolated objects

Translations / rotation coupling
Spin isomerism etc...

How about an endofullerene?

Endohedral Fullerenes! How do you make them?

- Molecular Surgery: 3 stages process



Encapsulation of Molecular Hydrogen in Fullerene C₆₀ by Organic Synthesis

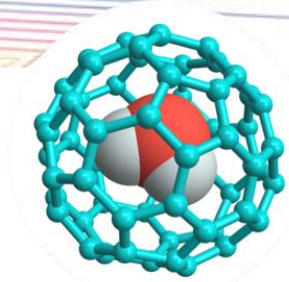
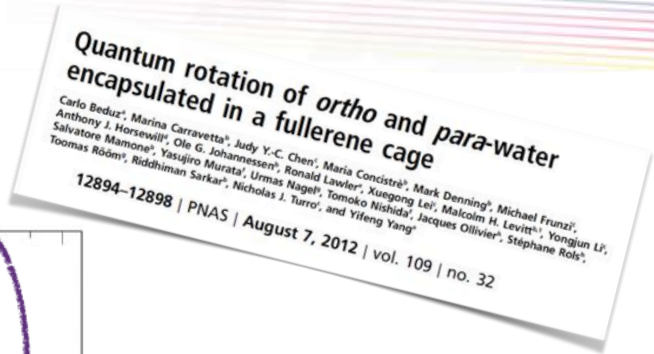
Koichi Komatsu,* Michihisa Murata, Yasujiro Murata

14 JANUARY 2005 VOL 307 SCIENCE

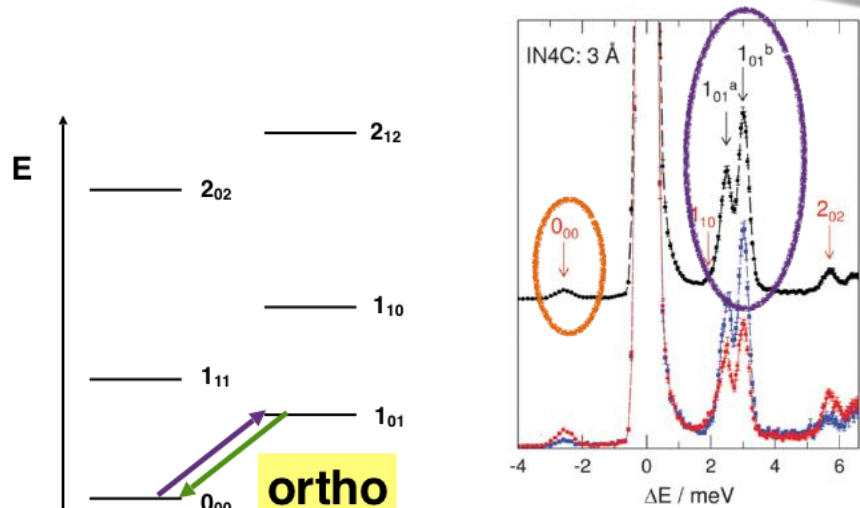
Problem is the scarcity of actual samples by the end of the surgery. Need High Flux neutron instruments ↔ ILL

The story so far

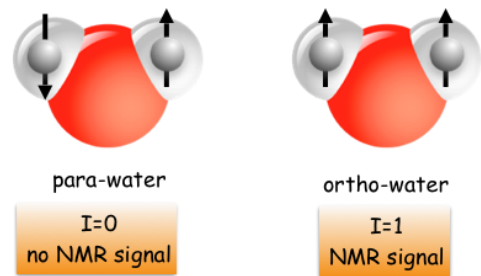
Why study them with neutrons?



A Single Molecule of Water Encapsulated in Fullerene C₆₀
 Kei Kurotobi and Yasujiro Murata*
 SCIENCE VOL 333 29 JULY 2011



ortho
para

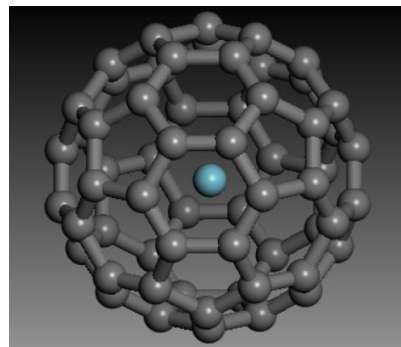


- INS allows the observation of modes which are forbidden in optical spectroscopies.
- In particular for diatomic molecules (H₂ or H₂O) neutrons allow transition between spin isomers

What's new?

“So what are you supposed to do?”

- INS Experiments data analysis for He@C₆₀ systems:
 - Numerical approach to calculate the potential energy surface
 - Develop a Hamiltonian to understand the physics of the system
 - Compare experimental spectra to simulated spectra
- More complex systems: CH₄@C₆₀ and C₂H₂@C₆₀
- Study the phase diagram of C₆₀



Noble gas systems He@C₆₀

“And away we go!”

- Why start by studying a He atom inside the cage? Couple of reasons:

Vibrational properties of noble gas endohedral fullerenes†

Fanica Cimpoesu,^{*a} Seitaro Ito,^b Hidekazu Shimotani,^c Hidenori Takagi^{bd} and Nita Dragoe^{*c}

Received 1st February 2011, Accepted 15th March 2011

DOI: 10.1039/c1cp20279k

Analysis of IR and Raman spectra of Ar@C₆₀ and Kr@C₆₀ shows that the incorporation of noble gas atoms causes a blue shift of low energy vibrations, which have radial character, and a red shift of higher energy ones which have a tangential character movement. The mechanism of these phenomena is explained on the basis of *ab initio* numerical experiments with DFT and MP2 procedures. Methodological discussions are advanced, altogether with a scheme for the estimation of the van der Waals interaction between fullerene and noble gas, based on the frequency shifts.

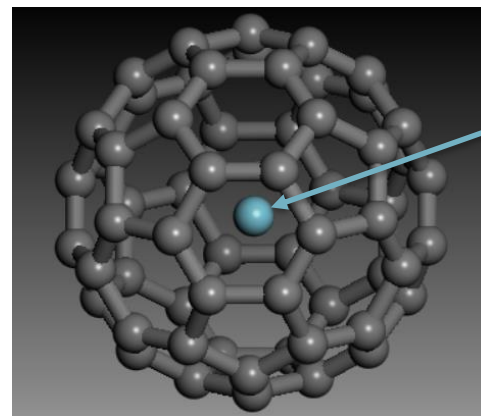
- Newly acquired experimental data on He@C₆₀

He@C₆₀? What's in there?

Because 60 atoms aren't enough of course!

- Moving on:
 - First, one needs to find the correct position for the new atom
 - Trial and error until finding the best functional

Functional	X (a.u)	Y (a.u)	Z (a.u)
PBE GGA+TS	-0.072	-0.054	0.0
PBE GGA+Grimme	-0.074	-0.0559	0.0



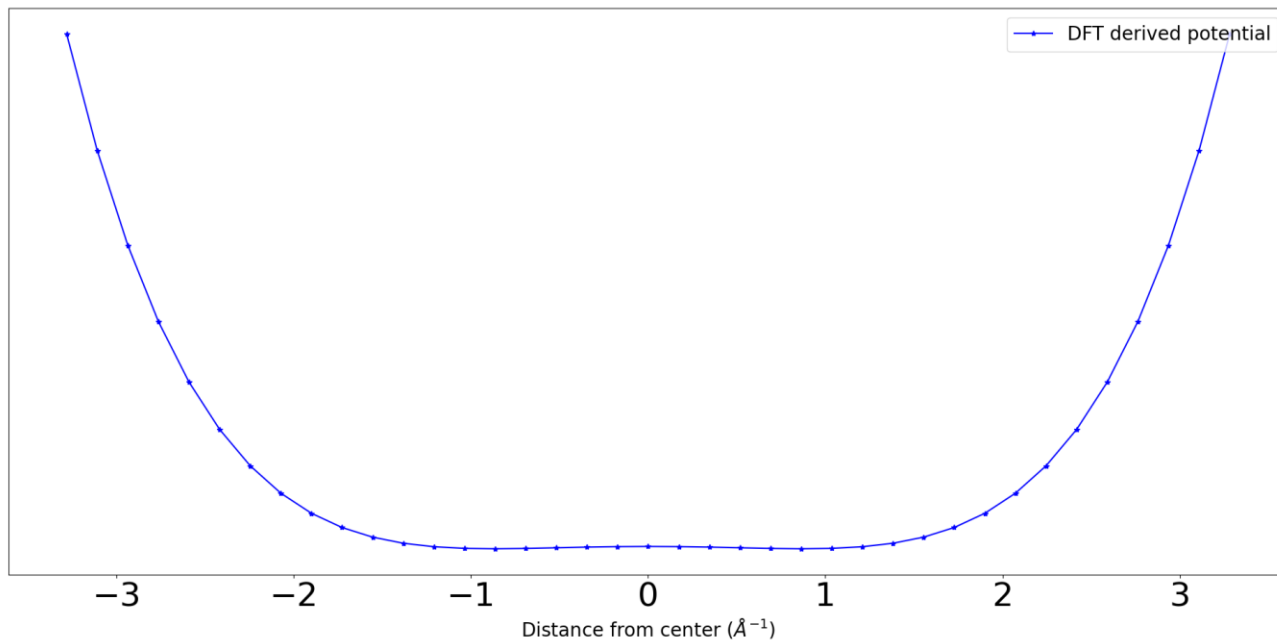
A new addition!
A Helium atom

Despite the central position of the He atom: Negative modes appeared!

Endofullerene: He@C₆₀

What does it look like inside?

- Fit of the potential inside the cage:



It's small but it's there! A double well potential!

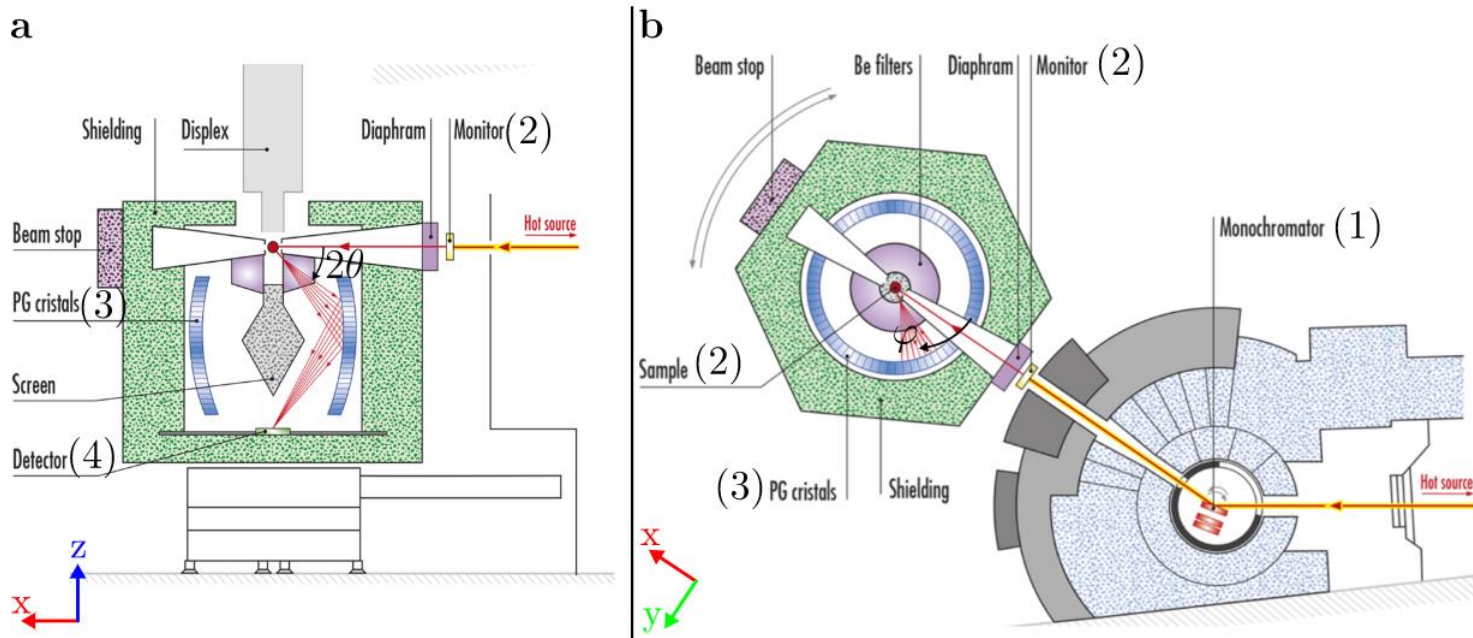
Endofullerene: He@C₆₀ Experimental data

Experimental data for ³He@C₆₀ on IN1-LAGRANGE

- How the data was acquired over 3 days on IN1:
 - A 1g sample of ³He@C₆₀ was analysed in an energy range of [8-150]meV at 2.6K
 - A mass matching blank fullerene was also analysed
 - The empty cell was also measured in order to subtract it
 - The important plot was the one remaining after subtracting the blank fullerene and the empty cell

Endofullerene: He@C₆₀ Experimental data

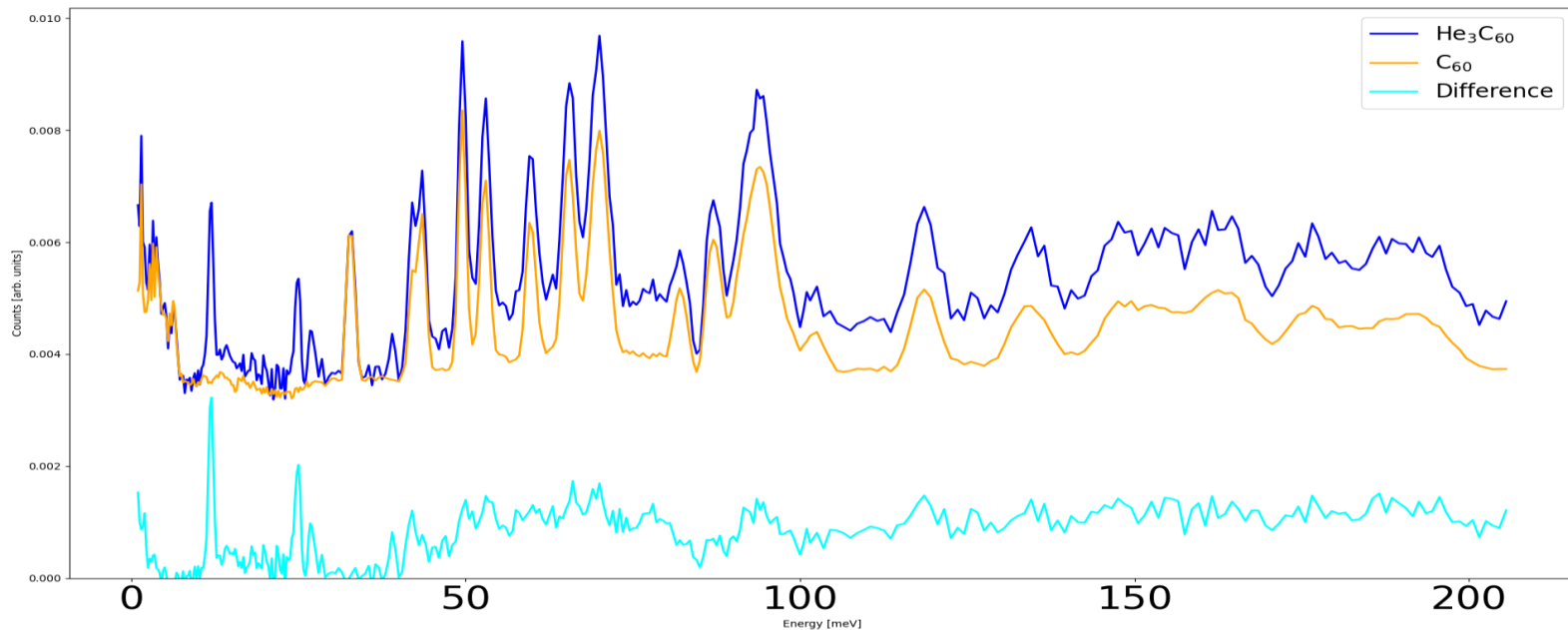
IN1-LAGRANGE setup



Endofullerene: He@C₆₀ Experimental data

Experimental data for 3He@C₆₀ on IN1-LAGRANGE

- How the data looked at the end:



Endofullerene: He@C₆₀ Simulations

Experimental data is here, now what?

- Now that we have observed new peaks (mainly the doublet around 25meV):
 - Simulate the positions of these transitions by using the DFT derived potential
 - Compare it to the Harmonic Oscillator (HO) model and to an anharmonic oscillator
 - Compare it to the Particle in a Box (PiB) model
 - Derive the INS intensities for all these models

Endofullerene: He@C₆₀ Simulations

How am I supposed to do that?

- Solve the Schrödinger equation in a numerical way for an arbitrary potential

$$-\frac{\hbar^2}{2m} \left(\frac{d^2 u(r)}{dr^2} - \frac{l(l+1)}{r^2} u(r) \right) + V(r)u(r) = Eu(r)$$

```
def calculate_angular_term(r):
    angular = 1 * (1 + 1) / r**2
    angular_term = sparse.diags((angular))
    return angular_term

def calculate_laplace_three_point(r):
    h = r[1] - r[0]

    main_diag = -2.0 / h**2 * np.ones(N)
    off_diag = 1.0 / h**2 * np.ones(N - 1)
    laplace_term = sparse.diags([main_diag, off_diag, off_diag], (0, -1, 1))
    return laplace_term

def calculate_potential_term(r):
    potential = 0.2852*r**2]
    potential_term = sparse.diags((potential))
    return potential_term

def build_hamiltonian(r):
    laplace_term = calculate_laplace_three_point(r)
    angular_term = calculate_angular_term(r)
    potential_term = calculate_potential_term(r)

    hamiltonian = -hbar**2 / (2.0 * m) * (laplace_term - angular_term) + potential_term

    return hamiltonian #Radial Part of the Schrodinger Equation
```


Endofullerene: He@C₆₀ Simulations

Experimental data vs DFT: A summary

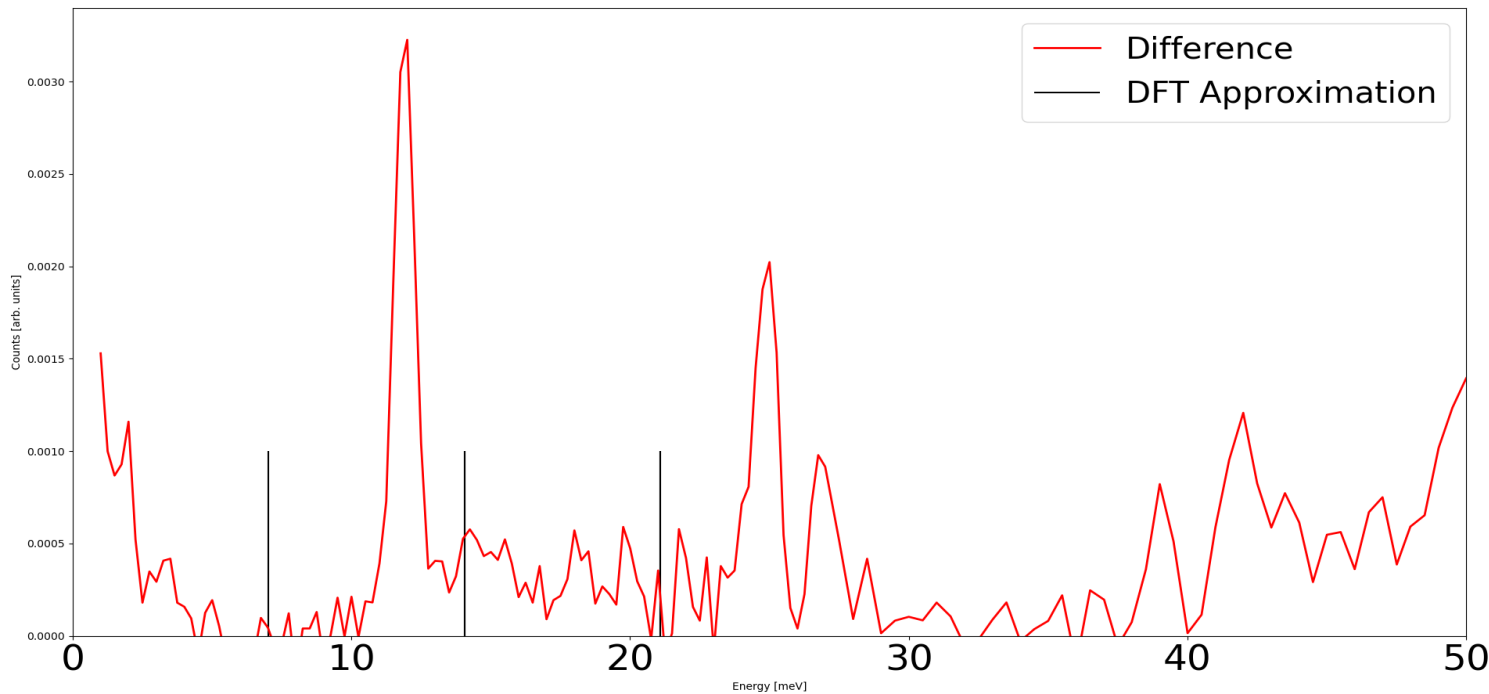
- Using the DFT potential: Fitted numerically to match the double well

Table 1: Exp vs DFT INS peaks

Exp peaks	DFT peaks	Difference (meV)
11.7	7.03	4.67
24.8	14.06	10.74
26.7	14.06	12.64
38.04	21.09	16.95
42	21.09	20.91

Endofullerene: He@C₆₀ Simulations

Experimental data vs DFT: A visual summary



- That doesn't look quite right!
- Perhaps DFT is wrong on this one?

Endofullerene: He@C₆₀ Simulations

Experimental data vs HO: Is it any better?

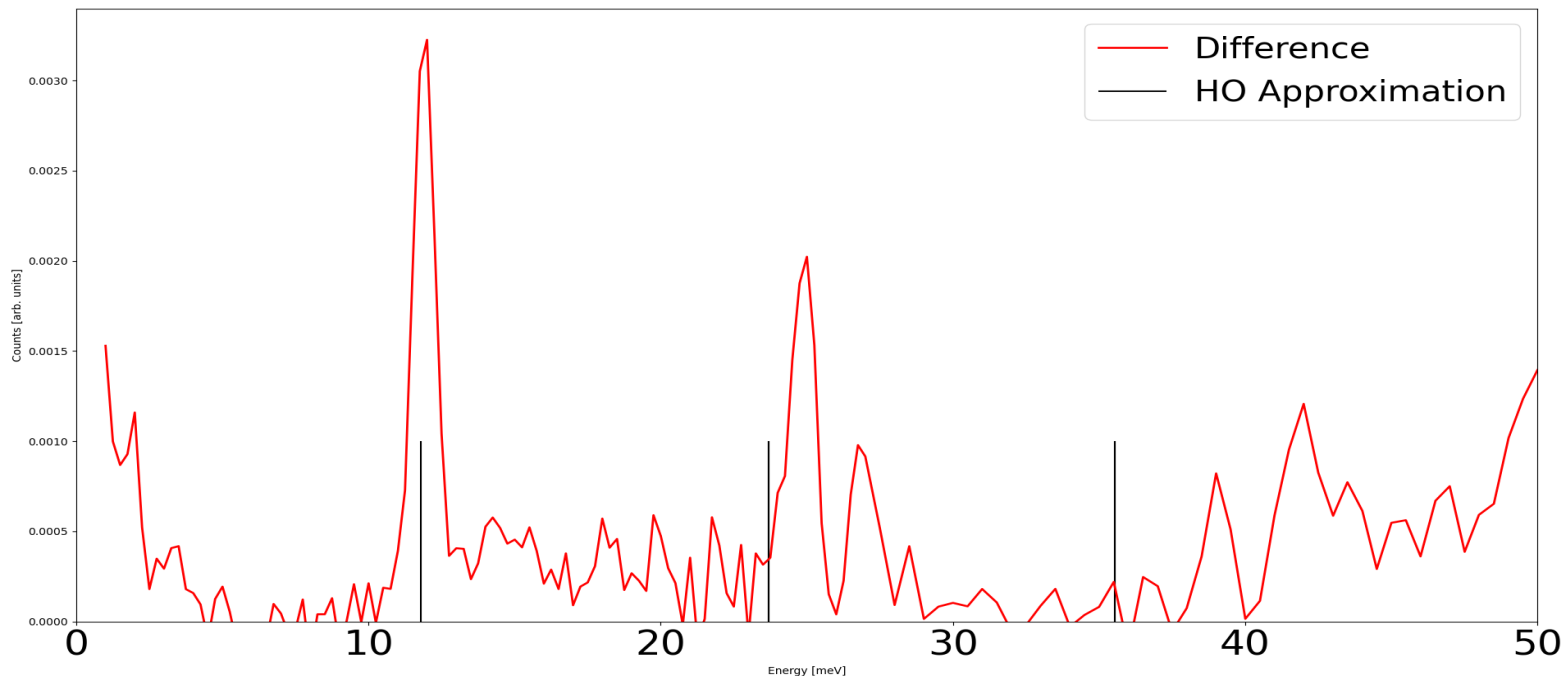
- Using the HO model: Fitted to match the first peak

Table 2: Exp vs HO INS peaks

Exp peaks	HO peaks	Difference (meV)
11.7	11.8	0.01
24.8	23.69	1.11
26.7	23.69	3.01
38.04	35.53	2.51
42	35.54	5.16

Endofullerene: He@C₆₀ Simulations

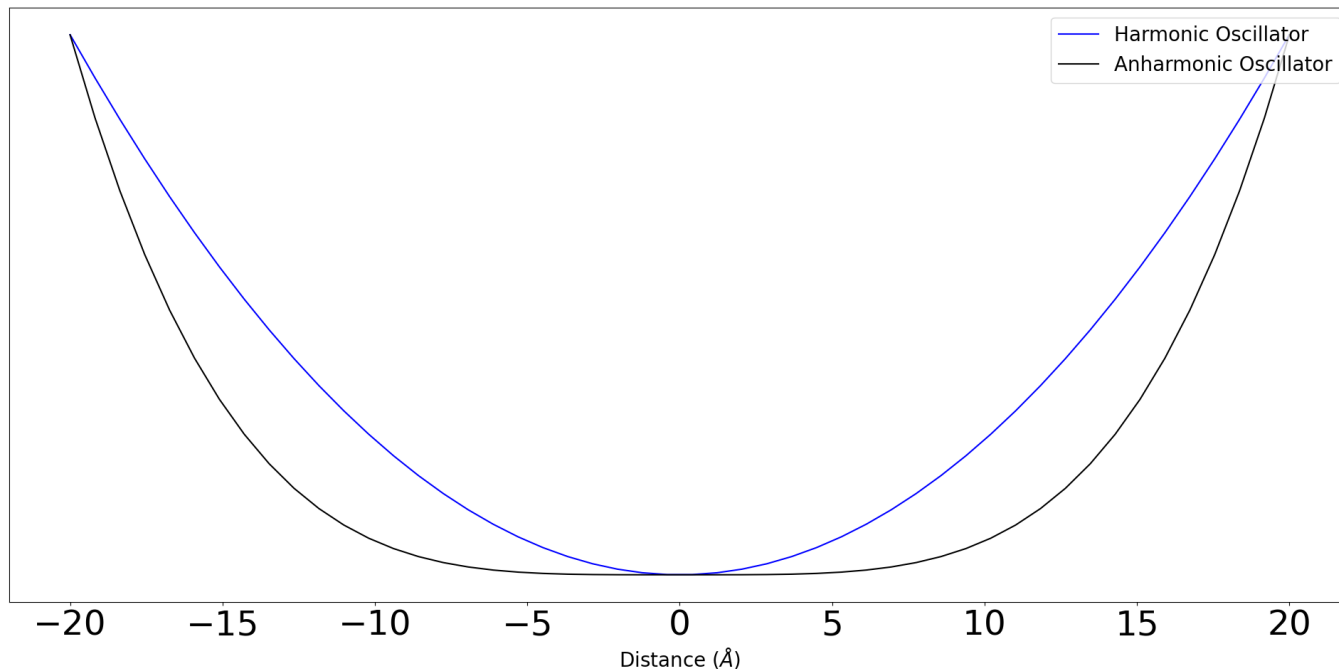
Experimental data vs HO: Slightly better version but not enough!



- Perhaps adding anharmonicity will give us a much better match?
- HO approach doesn't take into account the splittings.

Endofullerene: He@C₆₀ Simulations

HO vs Anharmonic Oscillator: What's the difference?



- Introducing a new term: r^4
- This should in theory split the l levels.

Endofullerene: He@C₆₀ Simulations

Experimental data vs the anharmonic oscillator: Finally getting somewhere!

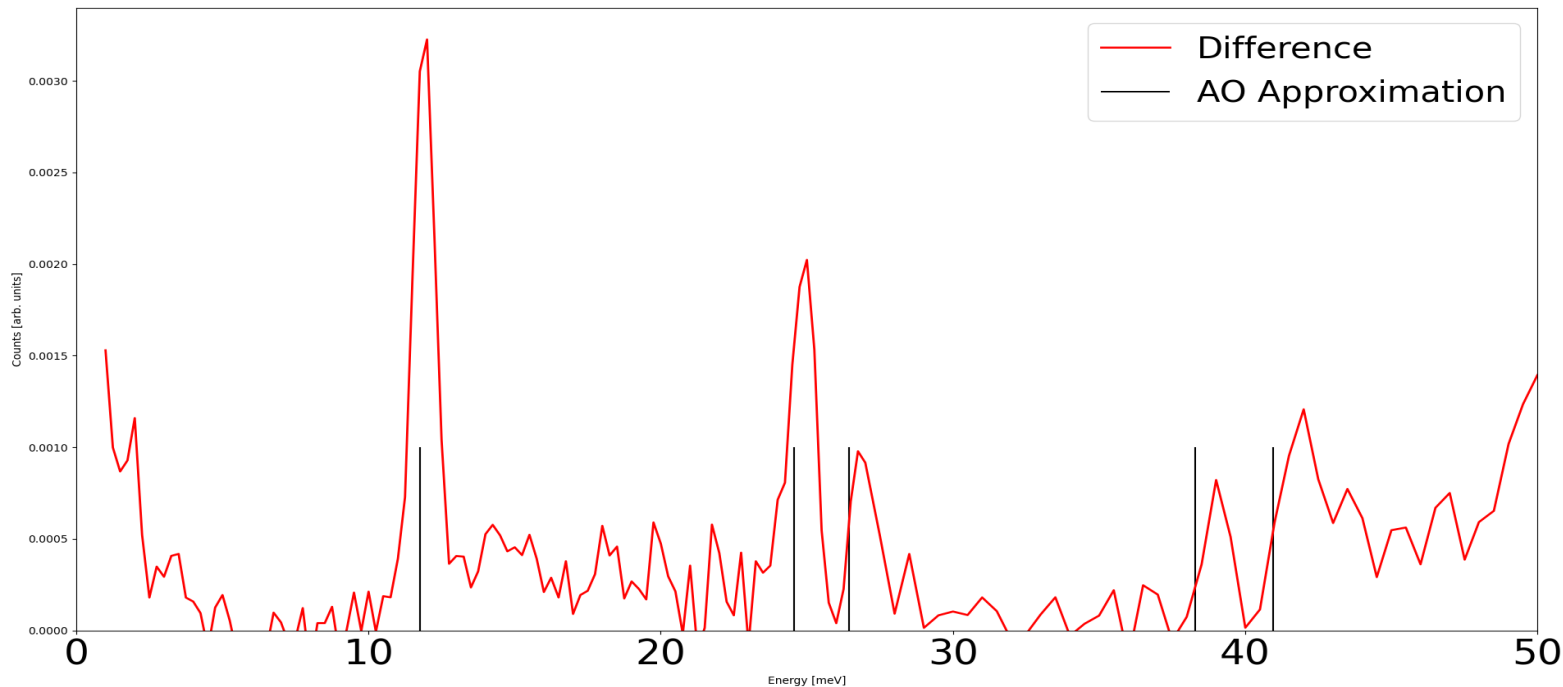
- Introducing the anharmonicity:

Table 3: Exp vs AO INS peaks

Exp peaks	AO peaks	Difference (meV)
11.7	11.75	0.05
24.8	24.57	0.23
26.7	26.43	0.27
38.04	38.28	0.24
42	40.97	1.03

Endofullerene: He@C₆₀ Simulations

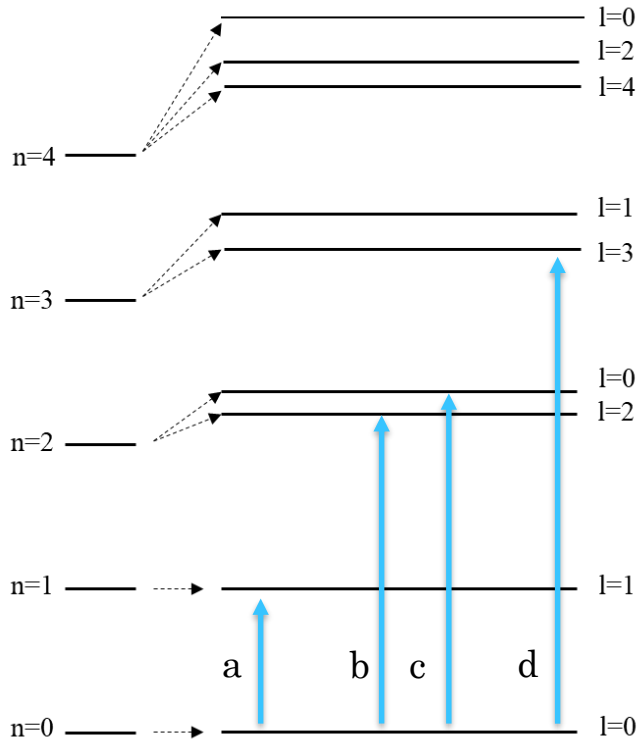
Experimental data vs AO: We're getting there!



- Introducing anharmonicity finally simulates the doublet correctly
- Match gets slightly worse when going higher in energy.

Endofullerene: He@C₆₀ Simulations

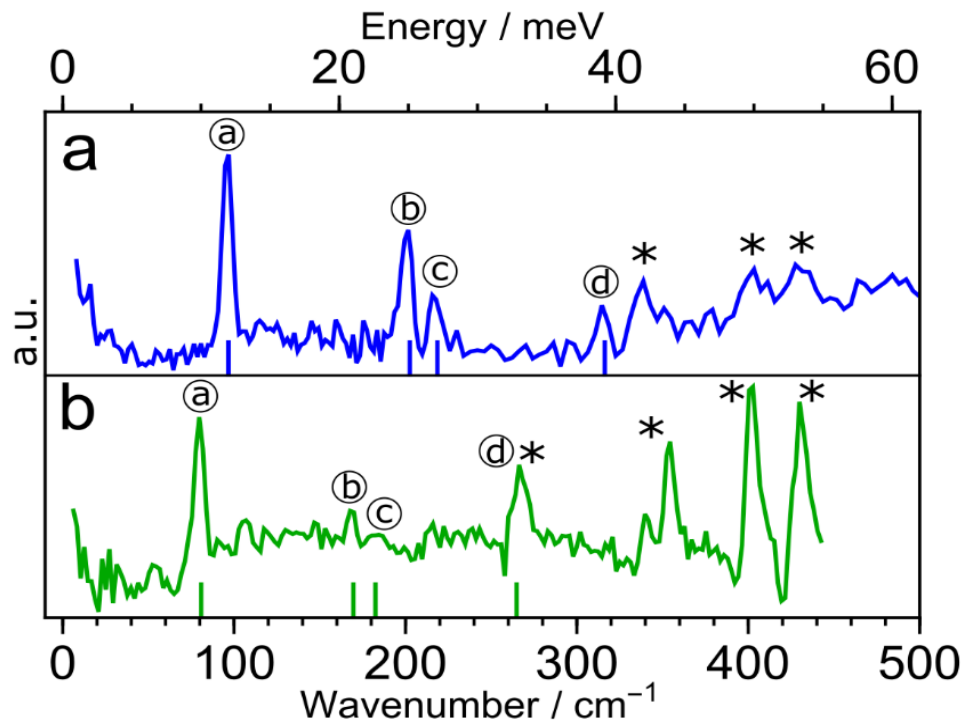
But how do we know those are actual transitions? Energy diagrams



- Introducing anharmonicity finally splits the energy levels compared to the harmonic approach
- The use of the HO quantum numbers and fine tuning the potential parameters has allowed a correct attribution of quantum numbers

Endofullerene: He@C₆₀ Simulations

Where do we go now?



- Using the anharmonic approach allowed us to attribute quantum numbers
- A higher order term should be added in order to get a better match with experimental data set

General remarks

What just happened?

- DFT has shown its limits when it comes to non bonded interaction by giving a double well potential for He
- The introduction of anharmonicity has given us a much better match but now we need an extra term to be added in order to get the closest match possible
- More beam time with a better resolution at higher energies is needed if we are to analyze the high energy part of the spectrum (Background noise + C60 modes make it difficult at the moment)
- More in depth analysis of the simulations by investigating the Q-dependence of each model



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