Rotations and vibrations of H_2O inside the fullerene cage: infrared study of $H_2O@C_{60}$

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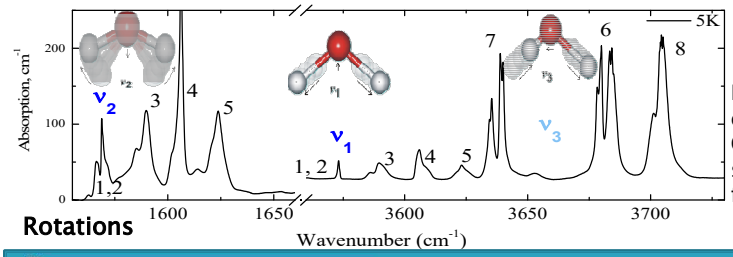
Water is the second molecule after hydrogen what has been trapped inside the cage of a C_{60} molecule by the molucular surgery method [1]. The water molecule rotation transitions were observed in the THz [2] and vibration-rotation transitions in the mid-IR range. The slow conversion between para (two proton spins couple to form a singlet, *I*=0) and ortho (triplet, I=1) water allowed us to record the time evolution of spectra and to separate ortho and para absorption lines of water. The exact mechanism of the ortho to para conversion is still not fully understood, and we studied the relaxation process at different temperatures and concentrations of $H_2O@C_{60}$ in order to clarify the kinetics.

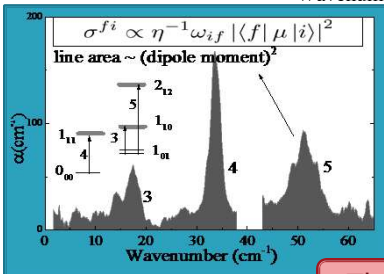
Objectives:
- H_2O interaction with the C_{60} cage
- Mechanism of ortho to para conversion

Vibrations



Pure vibrational transitions of water become partially allowed in C_{60}, so the spherical symmetry of bucky-ball is somehow distorted. We propose the existence of local electric field .

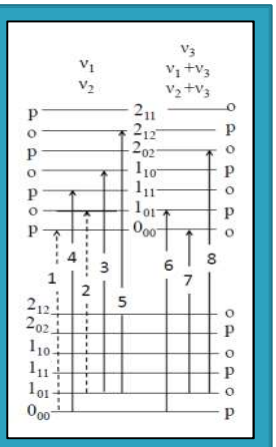
Rotations

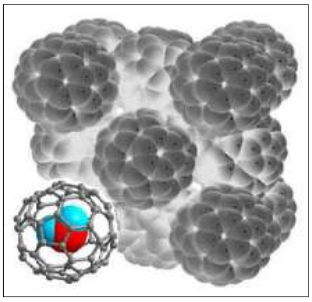


$$\mu_{C_{60}} = \frac{\mu_{gas}\sqrt{\eta_{C60}}}{\sqrt{6.7 \pm 1.0}} = 1.0 \pm 0.1\,\text{Debye}$$

The dipole moment of water in C_{60} is shielded by C_{60} electrons.

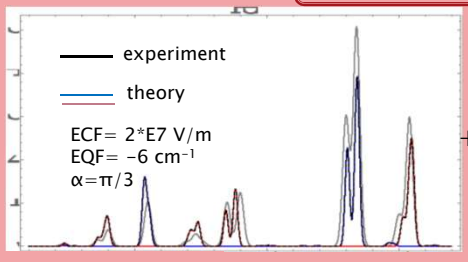
$$\mu_{gas} = 1.85\,\text{Debye}$$

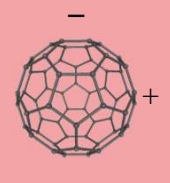




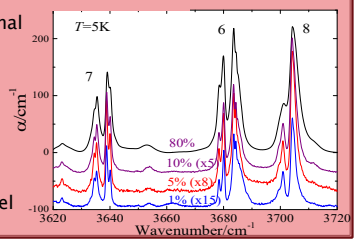
H_2O moleule inside the C_{60}

Theory and experiment

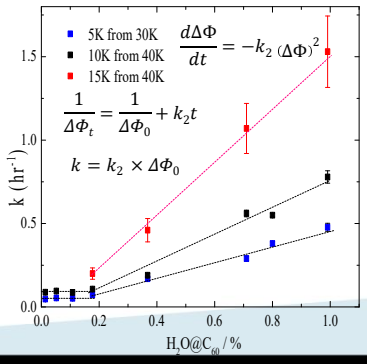




1. The intensity of pure vibrational transitions are reproduced by switching on the local dipolar electric field.
2. The splittings of rovibrational levels can be reached only if we add local quadrupolar electric field.
3. The existence of four 1_{01} level components remains unclear.



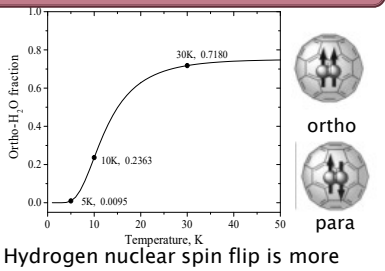
Ortho-para conversion of water molecule inside the C_{60}



$$\frac{d\Delta\Phi}{dt} = -k_2(\Delta\Phi)^2$$

$$\frac{1}{\Delta\Phi_t} = \frac{1}{\Delta\Phi_0} + k_2 t$$

$$k = k_2 \times \Delta\Phi_0$$



Hydrogen nuclear spin flip is more likely to occur when converting spin is surrounded by H_2O filled C_{60} cages, and when the final temperature is higher.

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Conclusion

The similarity of the rotation spectrum of caged water to water in the gas phase indicates that water is free to rotate in the C_{60} cage even at temperature as low as 4K. Spectral lines show a splitting of about 0.5 meV what is not compatible with the icosahedral symmetry of C_{60}. Adding dipolar and quadrupole electric fields allowed us to simulate this large splitting, but with only three (2+1) components, while experimentally recorded spectra clearly demonstrate 4 components for 1_{01} rotational level. Nuclear spin conversion in $H_2O@C_{60}$ is catalyzed by the neighboring rotating molecules.

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References

1. K. Kurotobi, Y. Murata, *A Single Molecule of Water Encapsulated in Fullerene C_{60}*, Science, **333** (2011), 613-616.
2. 2. Beduz et al., *Quantum rotation of* ortho *and* para*-water encapsulated in a fullerene cage*, PNAS **109** (2012), 12894.