# Potentials and energies of atoms and molecules inside $C_{60}$ cage

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Much of this work was stimulated by the discussion on the quantized rotation and ortho–para conversion of single water molecules permanently entrapped inside closed fullerene $C_{60}$ cages, see experimental and theoretical studies [1-4] and references therein. Of particular interest is, first, the observed splitting of the ground state of ortho-$H_2O$, raising the three-fold degeneracy into two states with degeneracy 2 and 1 [1] and, second, the enrichment of para water at low temperatures due to conversion of fullerene-encapsulated para water to ortho water [2]. In the present study we try to attribute both effects to interaction between water "vibrational" and rotational motions. Hereafter we denote the movement inside the cage as "vibrational", but it possess rotational momentum.

*Ab initio* calculations of He, Ne, Ar, HF, and $H_2O$ molecules entrapped inside $C_{60}$ cage are reported. We choose not only the water molecule, but molecules with different masses and rotational degrees of freedom. Program Orca was used on the B3LYP D3BJ TZV def2/J level of theory, where B3LYP is DFT functional, D3BJ is the Becke–Johnson damping version, TZV is valence triple-zeta basis set, and def2/J is universal auxiliary basis sets of Weigend.

The "vibrational" energies of three noble atoms inside C60 are represented in the table below, they are characterised by quantum numbers *n* and *L*, as in a hydrogen atom. The energies are given in cm$^{-1}$, they are calculated by using both WKB (Wentzel–Kramers–Brillouin) approximation and direct solution of the radial part of Schrëdinger equation.

| | He+$C_{60}$ | | | Ne+$C_{60}$ | | | Ar+$C_{60}$ | | |
|---|---|---|---|---|---|---|---|---|---|
| *n* | *L*=0 | *L*=1 | *L*=2 | *L*=0 | *L*=1 | *L*=2 | *L*=0 | *L*=1 | *L*=2 |
| 1 | 204.0 | | | 130.9 | | | 257.5 | | |
| 2 | 461.2 | 588.3 | | 304.8 | 440.5 | | 599.6 | 770.1 | |
| 3 | 715.6 | 846.8 | 981.3 | 478.9 | 615.2 | 741.4 | 940.3 | 1110.0 | 1279.3 |
| 4 | 982.6 | 1122.8 | 1267.0 | 654.3 | 792.0 | 919.8 | 1279.8 | 1448.8 | 1617.3 |

The Ne+$C_{60}$ system has almost the same reduced mass as $H_2O$+$C_{60}$, hence their "vibrational" energies should be similar. As it follows from the table, the "vibrational" transitions $n,L \rightarrow n',L'$ lies rather far from low-temperature rotational transitions in $H_2O$ and from vibrational transitions in $H_2O$. Note that the "vibrational" transitions obey usual selection rule $\Delta L=\pm 1$.

The movement of HF and $H_2O$ molecules inside $C_{60}$ was analysed similarly. In the model of "quick rotation" the movement in the case of HF changes from two-dimensional vibrational oscillator when F atom is close to the wall of the cage to the free rotation when F atom is close to the centre of gravity. More realistic model, in which H atom rotates with a speed comparable with the speed of F atom, permit rather small range of spherical θ angles for the rotation of H atom. Hence it was found that the fullerene cage shifts the rotation levels of the two molecules, in moderate agreement with experiment.

## References

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3. S. Mamone et al., *J. Chem. Phys.*, **2014**, 140, 194306
4. C. Beduz et al., *Proc. Natl. Acad. Sci. USA*, **2012**, 109(32), 12894