A Fully Coupled Quantum Treatment of Nanoconfined Systems: a Water Molecule inside a Fullerene C₆₀.

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Abstract

We implemented a systematic procedure for treating the quantal rotations by including all translational and vibrational degrees of freedom for any triatomic bent molecule in any embedded or confined environment, within the MCTDH framework. Fully coupled quantum treatments were employed to investigate unconventional properties in nanoconfined molecular systems. In this way, we facilitate a complete theoretical analysis of the underlying dynamics, that enables to compute the energy levels and the nuclear spin isomers of a single water molecule trapped in a C₆₀ fullerene cage. The key point lies on the full 9D description of both nuclear and electronic degrees of freedom, as well as a reliable representation of the guest-host interaction. The presence of occluded impurities or inhomogeneities due to noncovalent interactions in the inter-fullerene environment could modify aspects of the potential, causing significant

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coupling between otherwise uncoupled modes. Using specific n -mode model potentials, we obtained splitting patterns, that confirm the effects of symmetry breaking observed by experiments in the ground ortho-H₂O state. Further, our investigation reveals that the first rotationally excited states of the encapsulated ortho- and para-H₂O have also raised their three-fold degeneracy. In view of the complexity of the problem our results highlight the importance of accurate and computational demanding approaches for building up predictive models for such nanoconfined molecules.

1 Introduction

Encapsulation of molecules inside cage compounds has opened new opportunities to explore interesting properties of such guest-host systems with potential applications in nanoscience and nanotechnology.¹⁻⁵ Such nanoconfined systems have been the topic of broad research, focused on their different chemical and physical behavior compared with the bulk systems, as the confined molecules are subject to surrounding host medium, resulting specific unexpected effects on properties and dynamics of the guest moieties. So far, various types of nanocavities have been investigated, such as those of clathrate hydrates,⁶⁻¹⁵ rare gas nanodroplets,¹⁶⁻²¹ fullerenes,²² *etc.*

Trapping molecular complexes inside near-spherical cavities are the cases of the endohedral fullerenes. This is a fascinating research subject, that has been recently received particular attention, as a novel organic synthesis, namely molecular surgery by Murata and coworkers,²³⁻³⁰ made feasible the encapsulation of various molecules into fullerenes. Such synthetic route to endohedral fullerene complexes offers an opportunity to study their properties, and experimental inelastic neutron scattering (INS), far-infrared (FIR), and magic-angle-spinning nuclear magnetic resonance (MAS-NMR) spectroscopy techniques have been used to investigate unconventional quantum patterns. For example, several nanoconfined molecules exhibit new set of states, as a result of strong couplings between rotational and translational motions, and new selection rules have been applied to identify observed spectral

peaks with respect to those of an isolated molecule.^{27,31} Although, much has been learned about characterizing quantum confinement of molecular nuclear motion, several aspects of these features are still not fully understood. This is the case of the endohedral water fullerene ($\text{H}_2\text{O}@\text{C}_{60}$) complex, which has been recently synthesized,²⁵ and then characterized spectroscopically by INS, FIR and NMR techniques.^{26,32} The recorded INS and FIR spectra show numerous peaks assigned to transitions between ortho- and para- H_2O nuclear spin isomers, as well as excited rotational-translational states of them. Of particular interest is a surprising splitting of the ground ortho- H_2O state into two substates by about 4.2 cm^{-1} , that indicates a symmetry-breaking in the inter-cage environment. As mentioned, Murata and co-workers²⁵ have synthesized $\text{H}_2\text{O}@\text{C}_{60}$, through the molecular surgery technique, which consists of a series of chemical reactions, including the construction of an open-cage of an empty C_{60} fullerene cage, insertion of an H_2O molecule, and then restoration of the original closed-cage framework, retaining the encapsulated water molecule. On the one hand, diffraction x-ray methods have been used to determine the $\text{H}_2\text{O}@\text{C}_{60}$ structure, co-crystallized as $\text{H}_2\text{O}@\text{C}_{60}(\text{NiOEP})_2$, with the oxygen atom positioning in the center of the C_{60} cage, while the hydrogen atoms are pointing towards the Ni atoms. Although, such finding may indicate some sensitivity to the external to the fullerene molecular environment, the authors have concluded,²⁵ on the basis of NMR, FIR and UV/Vis spectroscopic analysis, that the H_2O molecule is electrochemically stable under the hydrophobic environment inside C_{60} . On the other hand, earlier and current electronic structure studies³³⁻³⁸ indicate that the encaged H_2O molecule is not chemically isolated, and there are significant noncovalent interactions within the cage, causing the elongation of the OH bonds, decrease in the HOH angle, off-center location of the trapped water molecule, and a notable reduction of the dipole moment of the H_2O molecule upon confinement in the C_{60} cage.

Recent studies have also been carried out elaborating a variety of theoretical models for explaining the experimental observations. Felker and Bačić have reported³⁹ a 6D approach to the problem of a water molecule in a fullerene, considering that the vibrations of the guest

molecule do not affect considerably the rotational scenario. They computed and assigned the translational and rotational states up to 400 cm^{-1} . However, the experimental observation of the splitting for the lowest $j=1$ H_2O states remained unresolved from the theoretical point of view in their 6D study. In the same vein, more recently the same authors have investigated the effect of electric dipole-dipole interaction by considering the $\text{H}_2\text{O}@\text{C}_{60}$ dimer forming by two neighbor occupied C_{60} cages,⁴⁰ while in an other study,⁴¹ a quadrupolar model case where a central occupied C_{60} cage is surrounded by twelve nearest-neighbor empty C_{60} cages^{41,42} have been considered. In these latter articles,^{41,42} the authors carried out first-order perturbation theory and variational calculations, and they observed the splitting of the $j=1$ level of H_2O , only for the P orientation ordering of the C_{60} cages. In addition, by employing their quadrupole model they have calculated splittings for the $\text{H}_2@\text{C}_{60}$ and $\text{HF}@\text{C}_{60}$ species, and they draw a linear scaling relationship between the ground $j=1$ levels' splittings of these endofullerenes, while the splittings of the excited levels have been found to highly depend on the nature of excitations involved.⁴² In turn, they also reported low-temperature weighted-sum ($0.15\text{H}+0.85\text{P}$) IR spectra in quantitative agreement with the experimental ones for the $\text{H}_2@\text{C}_{60}$ and $\text{HF}@\text{C}_{60}$, while for the $\text{H}_2\text{O}@\text{C}_{60}$ their simulated spectrum predicts features that could be potentially observed experimentally, and could serve for future tests of their electrostatic model. By considering such findings as strong evidence the authors concluded⁴² that the electrostatic/quadrupole interaction between the guest molecule and the 12 nearest-neighbor empty C_{60} cages is the main source of the symmetry breaking in these systems from their translational-rotation calculations.

From theoretical point of view, the ability to provide reliable interpretation of nanoconfined or embedded molecules relies on the development of methodology for rigorous full dimensional quantum simulations. The computation of the translational, vibrational and rotational levels is a difficult problem to handle as dimensionality of the system increases, although of great importance in order to understand the properties and interactions of such guest-host systems. The nature of the guest-host interactions may modify the behavior of

the gas-phase systems, by mixing the otherwise uncoupled modes of the trapped molecule, and thus, a complete description of the whole dimensionality should be used instead. Such theoretical approaches could provide very detailed information, so it is important to exploit modern techniques taking advantage of their capabilities for carrying out full-dimensional quantum calculations for nanoconfined molecules. A promising method for dealing with the nuclear dynamics in multidimensional systems is the multiconfiguration time-dependent Hartree (MCTDH).^{43–45}

Within the present study, we tackle the full problem by developing a strategy to handle with the exact kinetic energy operator, as well as the representation of the multidimensional potential energy surface for any triatomic bent molecule in any embedded or confined environment. In turn, we setup the molecular Hamiltonian, within the MCTDH framework, and fully coupled 9-dimensional (9D) quantum calculations for the $\text{H}_2\text{O}@\text{C}_{60}$ endofullerene including all translational, vibrational and rotational degrees of freedom were carried out. We speculate for possible terms in the potential expansion that could explain the nature of the interaction causing the symmetry breaking observed in the $\text{H}_2\text{O}@\text{C}_{60}$ endofullerene. A thorough understanding of the splitting of the ground ortho- H_2O state could provide insights on inter-/intra-molecular interactions and mode couplings/symmetry breaking of such nanoconfined systems. Further, benchmark results are also desirable for quantitative checks of any approximated methods to be designed for dealing with higher dimensional systems.

The article is organized as follows: in the next section we outline the computational details of the MCTDH calculations. We setup the Hamiltonian operator for a triatomic bent nanoconfined molecule, and discuss the accuracy of the potential energy expansion within the MCTDH approach. Section 3 includes all computational results of the ground and lower rotationally excited levels, the corresponding splittings for the $\text{H}_2\text{O}@\text{C}_{60}$ endofullerene, while comparison with previous theoretical and experimental data, as well as possible origins for the breakdown of the endofullerene’s symmetry are also discussed. The article ends with the summary and concluding remarks.

2 Computational details

2.1 Hamiltonian Operator

In Fig. 1 we display the coordinate system used to represent the $\text{H}_2\text{O}@C_{60}$. We employed the set of (R_1, R_2, γ) internal valence coordinates to describe the water molecule (see right panel of Fig. 1), with $\mathbf{R}_1$ and $\mathbf{R}_2$ being the vectors joining the two hydrogen atoms with the oxygen atom, and γ being the angle between the vectors $\mathbf{R}_1$ and $\mathbf{R}_2$. The position of the H_2O molecule inside the fullerene is described by the spherical polar coordinates (R, β, α) of its center of mass (see left panel of Fig. 1). The Z axis of the body-fixed (BF) frame is chosen to be parallel to $\mathbf{R}_1$, while $\mathbf{R}_2$ is lying in the XZ -plane. So the final set of coordinates is $\mathbf{q}=(R, \beta, \alpha, R_1, R_2, \gamma, \phi, \theta, \chi)$ with (ϕ, θ, χ) being the three Euler angles connecting the body-fixed and space-fixed (SF) frames.

Figure 1: Schematic representation of the (R_1, R_2, γ) valence coordinates of the H_2O system, the (R, β, α) spherical coordinates of the center of mass of the water molecule in the SF coordinate system, and the three Euler angles (ϕ, θ, χ) connecting the SF and BF coordinate systems.

As a first step for any quantum treatment the Hamiltonian, $\hat{H} = \hat{T} + V(\mathbf{q})$, of the system was derived following procedures of Refs.^{46,47} The expression of the exact kinetic energy operator in the internal full-dimensional coordinate system is given in the supplementary

material, while the potential term was constructed as:

$$V(\mathbf{q}) = V_{H_2O}(R_1, R_2, \gamma) + V_{H_2O-C_{60}}(\mathbf{q}). \quad (1)$$

The first term, $V_{H_2O}(R_1, R_2, \gamma)$, in Eq. 1 corresponds to the spectroscopically determined water monomer potential of Ref. 48, while the second one, $V_{H_2O-C_{60}}(\mathbf{q})$, represents the interaction of the water molecule with the fullerene C_{60} cavity. This intermolecular (semiempirical) potential was constructed as a sum of pairwise Lennard-Jones (LJ) type interactions between each oxygen/hydrogen atom of water molecule and each carbon atom of C_{60} ,

$$V_{H_2O-C_{60}}(\mathbf{q}) = \sum_{i=1}^{60} V_{H_2O-C_i}^{LJ}(\mathbf{q}) \quad (2)$$

The parameters of the LJ-potentials have been obtained by fits to DFT-SAPT *ab initio* calculations for the graphene-water system, as given in Ref. 49. Unfortunately, there is no *ab initio* reduced or full dimensional intermolecular potential available in the literature for the $H_2O@C_{60}$ system, so this potential form has been also used to model the H_2O-C_{60} interaction in recent 6D calculations,³⁹ as well as in earlier molecular dynamics (MD) simulations.⁴⁹

2.2 MCTDH calculations

The MCTDH method^{45,50} was used to solve the time-dependent Schrödinger equation for distinguishable particles. The multidimensional wavefunction is written as sum-of-products form of low dimensional functions, called single particle functions (SPFs), and are represented as a linear combination of time-dependent primitive, commonly discrete-variable-representation (DVR), basis functions. Such approach allows, in principle, to treat systems with higher dimensionality. Its computational efficiency relies in building the Hamiltonian in product form, and in calculating its matrix elements as a sum of products of monoparticle integrals. Usually, kinetic energy operators are in sum of products or compact form, that leads to faster convergence, while potential energy are not, thus must be written in order to achieve

the desired efficiency of the method. Within the MCTDH framework, the POTFIT⁵¹ is the default procedure to fit the multidimensional PES to a sum of products of one-dimensional operators, called natural potentials. However, POTFIT approach is restricted to systems up to 6-7 degrees of freedom. So, for treating larger dimensionality systems alternatives, such as the multigrid POTFIT,⁵² and n -mode representation of the PES,⁵³ should be considered. Therefore, we adopted a seven mode combination scheme, taking into account the strongly coupled coordinates from the 9 degrees of freedom of the H₂O@C₆₀ system, as, $Q_1 = R$, $Q_2 = [\beta, \alpha]$, $Q_3 = \theta$, $Q_4 = [\phi, \chi]$, $Q_5 = R_1$, $Q_6 = R_2$, and $Q_7 = \gamma$. Then, the 7-mode representation of the potential reads,

$$V_M(Q_1, Q_2, \dots, Q_7) = V^{(0)} + \sum_{i=1}^7 V_i^{(1)}(Q_i) + \sum_{i \neq j}^7 V_{ij}^{(2)}(Q_i, Q_j) + \dots + \sum_{i \neq j \neq k \neq \dots}^7 V_{ijk\dots}^{(7)}(Q_i, Q_j, Q_k, \dots,). \quad (3)$$

where, $V^{(0)}$ is the potential value at a reference configuration, $V^{(1)}$ are the intra-mode terms calculated by keeping the remaining modes at their reference geometry, $V^{(2)}$ are the mode-mode terms, while higher $V^{(n)}$ terms are the n -mode (3 up to 7) correlations between the 7 different modes. The 7-mode expansion, V_M , in Eq. 3 is the exact representation of the H₂O@C₆₀ PES. However, by counting the required potential grid, one can see that for an affordable full 9D calculation the total number of points should be reduced. Thus, we proceeded to truncate the n -mode expansion, by employing different approximations to the $V_{H_2O-C_{60}}$ potential. We should note that as we carried out MCTDH calculations from 6 up to 9 degrees of freedom, we have introduced a 4-mode scheme for the reduced 6D system, up to a 7-mode one for the 9D problem. Therefore, we derived n -mode selected representations as follows.

$$V^{6D}(Q_1, Q_2, Q_3, Q_4) = V_{5D}(Q_2, Q_3, Q_4) + \Delta V_{6D_R}(Q_1, Q_2, Q_3, Q_4) \quad (4)$$

$$V^{7D\gamma}(Q_1, Q_2, Q_3, Q_4, Q_7) = V^{6D}(Q_1, Q_2, Q_3, Q_4) + \Delta V_{6D_\gamma}(Q_2, Q_3, Q_4, Q_7) \quad (5)$$

$$V^{8D^{R_1, R_2}}(Q_1, Q_2, Q_3, Q_4, Q_5, Q_6) = V^{6D}(Q_1, Q_2, Q_3, Q_4) \quad (6)$$

$$+ \Delta V_{6D_{R_1}}(Q_2, Q_3, Q_4, Q_5) + \Delta V_{6D_{R_2}}(Q_2, Q_3, Q_4, Q_6)$$

$$V^{9D}(Q_1, Q_2, Q_3, Q_4, Q_5, Q_6, Q_7) = V^{8D^{R_1, R_2}}(Q_1, Q_2, Q_3, Q_4, Q_5, Q_6) \quad (7)$$

$$+ \Delta V_{6D_\gamma}(Q_2, Q_3, Q_4, Q_7)$$

$$V_{R_v}^{9D^{vib}}(Q_1, Q_2, Q_3, Q_4, Q_5, Q_6, Q_7) = V_{6D}(Q_1, Q_2, Q_3, Q_4) + \Delta V_{6D_{vib}}(Q_1^v; Q_3, Q_4, Q_5, Q_6, Q_7) \quad (8)$$

According to the n -mode representation, in all cases (see Eqs.4- 8) the degrees of freedom not included in the parenthesis are fixed at their equilibrium values. For example, in the $V^{6D}(Q_1, Q_2, Q_3, Q_4)=V^{6D}(R, \beta, \alpha, \phi, \theta, \chi)$ the internal water coordinates R_1, R_2 and γ are kept in their equilibrium positions, while in the $V_{5D}(Q_2, Q_3, Q_4)=V_{5D}(\beta, \alpha, \phi, \theta, \chi)$ term, the R coordinate is fixed at its calculated average value 0.207 bohr. To take into account the effect of the internal coordinates of the water molecule and the position of its center of mass, we select to include the $\Delta V_{6D_{Q_i}}(Q_i, Q_2, Q_3, Q_4)=\Delta V_{6D_{Q_i}}(Q_i, \beta, \alpha, \phi, \theta, \chi) = V_{6D_{Q_i}}(Q_i, \beta, \alpha, \phi, \theta, \chi) - V_{5D}(\beta, \alpha, \phi, \theta, \chi)$ with $i = 1, 5, 6, 7$ terms in the expansion.

We should emphasize that the V^{6D} expression in Eq. 4 corresponds to the exact potential representation of the 6D system, while the remaining expressions are reduced and full dimensional potentials, with the V^{9D} forms in Eqs. 7 and 8 being approximations, that have the full dimensionality of system to deal with the computational problems associated with large potential grids involved in the MCTDH and/or any other quantum calculation. Therefore, for studying the effects of the increasing dimensionality in the potential surface, different approaches within the n -mode selected terms representation were made by freezing the corresponding coordinates. Each of these n -mode selected terms of the expansion in

Eqs. 4- 8, as well as the $V_{H_2O}(R_1, R_2, \gamma)$ in Eq. 1 were converted in the sum of products form using the POTFIT code,⁵¹ as implemented in the MCTDH package.⁵⁰

Moreover, the effect of the potential's anisotropy is studied by using the $V_{R_v}^{9D^{vib}}$ potential expression (see Eq. 8), that takes into account the combined coupling of the 3 vibrational degrees of freedom R_1, R_2 and γ with the rotational ones ϕ, θ and χ by including the term $\Delta V_{6D^{vib}} = V_{6D_{R_1, R_2, \gamma}}(R_1, R_2, \gamma, \phi, \theta, \chi) - V_{3D}(\phi, \theta, \chi)$. In this case, we choose the reference configuration for the Q_1^v mode to correspond to R values of 0.0, 0.2 and 0.4 bohr, instead of its average value used in the other n -mode representations in Eqs. 4-7.

Figure 2: Convergence of the indicated n -mode potential expansions to the full dimensional $V(\mathbf{q})$ potential.

The error of each n -mode potential approaches, V^{6D} , $V^{7D\gamma}$, $V^{8DR_1R_2}$, V^{9D} , $V^{9D^{vib}}$ (see Eqs. 5-8), was checked by comparison with the original $V(\mathbf{q})$ potential (see Eq. 1) at a grid of 10^9 points along all 9 coordinates. In Figure 2 we show the convergence of each potential form, given in Eqs.4- 8, with respect to the original PES of Eq. 1. In Fig. 2 we depict the percentage of configurations as a function of the mean absolute error (MAE) value with respect to the original $V(\mathbf{q})$ potential for each of the expressions in Eqs. 4-8. We have calculated the average energy differences of the total number of 10^9 points to be 13.19, 12.99,

3.00, and 1.82 and 4.88 cm^{-1} for the V^{6D} , $V^{7D\gamma}$, $V^{8D^{R_1,R_2}}$, V^{9D} , and $V_{0.0}^{9D^{vib}}$, respectively. As we can see in Fig. 2, the effect of including the $\Delta V_{6D_{R_1}}$ and $\Delta V_{6D_{R_2}}$ terms clearly improves the quality of the potential, while the influence of the ΔV_{6D_γ} term is much smaller. The potential $V_{0.0}^{9D^{vib}}$ also improves the performance of the V^{6D} approach but it is still not as efficient as the V^{9D} that has the best performance compared to the original potential of Eq. 1.

Previous studies have reported binding energy values for the $\text{H}_2\text{O}@\text{C}_{60}$ between -0.09 to -11.5 kcal/mol,^{33–36,38,54,55} with the more recent ones obtained from DFT SAPT,⁵⁴ PBE0,³⁵ and B3LYP³⁶ first-principles calculations predicted energies of -7.36, -6.36, and -0.09 kcal/mol, respectively. The well-depth of the present semiempirical PES is -2229.79 cm^{-1} (-6.375 kcal/mol), in close agreement with those values from the DFT/PBEO calculations.³⁵ In Fig. 3 we show 1D potential curves as a function of R distance for the water molecule moving between two fixed diagonal carbon atoms of the C_{60} cage. The curves are obtained by minimizing the potential energy at each R distance between two diagonal carbon atoms of the C_{60} . The potential energy values obtained from the present V^{9D} and V_{vib}^{9D} semiempirical PESs are compared with relative total energies from constrained (see black solid line) and unconstrained (see black dashed line) PBE0/6-31G(d,p) DFT calculations.³⁵ One can see various differences between the semiempirical and first-principles DFT/PBE0 potential curves,³⁵ especially in the case of unconstrained calculations, while in the right side panel of the figure we show the minimum energy structures obtained from V^{9D} and V_{vib}^{9D} semiempirical PESs, as well as from the M06-2X/6-311G(2d,p) and B97-D3/def2-SVP DFT calculations.^{25,35,38} We should also note that using the semiempirical model potentials from Eq. 2 the water molecule is considered fixed at its equilibrium geometry, while previous reported electronic structure calculations^{33–35,38} predicted elongation of the OH bonds (R_1 and R_2) and a slightly smaller bond angle, γ , by about 0.01 Å and 1° , respectively, as well as an off-center location of the trapped water molecule (see Fig. 3). As we mentioned above the n -mode representation of the total 9D PES (see Eqs. 1 and 4–8), takes into account the combined coupling of the vibra-

tional and rotational/translational degrees of freedom, with the $V_{R_v=0.4}^{9D^{vib}}$ potential showing anisotropy behavior (see Fig. 3), although significantly smaller than the ones predicted by the recent DFT calculations³⁵ (see Fig. 3).

Figure 3: Minimum potential energy curve (left panel) as a function of R obtained for the rigid V^{9D} and V_{vib}^{9D} semiempirical PESs (colored solid lines), as well as from unconstrained (see **a** line) and constrained/rigid (see **b** line) PBE0/6-31G(d,p) calculations as reported in Ref.³⁵ (see text). Top and side views of minimum potential energy structures of $H_2O@C_{60}$ from the indicated semiempirical model PESs and available DFT calculations from Refs.^{25,38}

In turn, once we set up the Hamiltonian operator, we should also define the basis sets and the parameters of the grid for evaluating its matrix elements. In Table 1, we summarize the range, number and type of primitive basis set used in the MCTDH calculations for each coordinate, where HO refers to the harmonic oscillator (Hermite) discrete variable representation (DVR) basis, *Leg* for the associated Legendre functions, *PLeg/exp* stands for the two-dimensional Legendre DVR basis and exp for the exponential (periodic boundary condition) DVR basis.

Nuclear quantum bound state computations were carried out employing the *block improved relaxation* method (BIR)⁵⁶ implemented in the Heidelberg MCTDH package,^{43,44,50} We started with a block of 10 initial states, which converged collectively to 10 eigenstates, including the ground and the nine lower excited states. Such calculations were required 4,

Table 1: Primitive DVR basis set used in the MCTDH and POTFIT calculations. Bond distances in bohr and angles in rad.

Coordinate	R	β	α	ϕ	θ	χ	R_1	R_2	γ
No/Type	25/HO	35/ <i>PLeg</i>	35/exp	35/exp	35/ <i>Leg</i>	35/exp	25/HO	25/HO	25/ <i>Leg</i>
Grid range	(0.0,0.7)	(0, π)	(0,2 π)	(0,2 π)	[0,2 π)	(0,2 π)	(1.3,2.4)	(1.3,2.4)	(1.22,2.63)

9, 2, 2, 3, 12, and 60 SPFs in each $Q_{i=1-7}$ combination mode, respectively.

3 Results and Discussion

Table 2: Comparison of the ground state, E_0 , and the 9 lowest rotationally excited states from 6D and 9D MCTDH calculations (This work) with previous rigid rotor and 6D theoretical and experimental data: ^(a) from Ref. ³⁹ and ^(b) from Ref. ^{26,32}

Transition: Quantum states	Theory		Experiment
	This work (6D/7D/8D/9D)	Free rotor/6D ^(a)	INS/FIR ^(b)
$E_0: 0_{00}$	2649.44/2649.43/2667.96/2667.97 -1985.94/-/-/-1967.41	- -/-1987.57	- -
1: $0_{00} \leftrightarrow 1_{01}^{a,a'}$	23.72/23.72/23.76/23.76	23.80/23.74	18.6 $\pm$ 0.8/-
2: $0_{00} \leftrightarrow 1_{01}^b$	23.75/23.75/23.79/23.79	23.80/23.74	23.4 $\pm$ 0.8/-
4: $0_{00} \leftrightarrow 1_{11}^{a,a'}$	36.50/36.48/36.68/36.66	37.16/36.50	-/37 $\pm$ 5
4: $0_{00} \leftrightarrow 1_{11}^b$	36.51/36.49/36.69/36.66	37.16/36.50	-
$0_{00} \leftrightarrow 1_{10}^b$	41.80/41.79/41.79//41.95	42.39/41.85	-
$0_{00} \leftrightarrow 1_{10}^{a,a'}$	41.87/41.86/42.03/42.02	42.39/41.85	-
3: $1_{01} \leftrightarrow 1_{10}$	19.42-19.62/18.85-20.08	18.59/18.11	-/20 $\pm$ 5
$1_{01}^a \leftrightarrow 1_{11}$	12.78/12.76/12.92/12.90	13.36/12.76	16.98 $\pm$ 0.8/-

In Table 2 we show the results from the coupled 6D, 7D, 8D and 9D quantum calculations using the potential forms V^{6D} , $V^{7D\gamma}$, $V^{8D^{R_1,R_2}}$, V^{9D} (see Eqs. 4-7), respectively. The ground vibrational state is found at energies of $E_0^{V^{6D}}=2649.44$ cm⁻¹ for the exact V^{6D} potential representation (see Eq. 4), and $E_0^{V^{9D}}=2667.97$ cm⁻¹ for the most accurate approach of the V^{9D} potential form (see Eq. 7). For a direct comparison with the 6D results of Ref. ³⁹ we should include the zero-point energy (ZPE) for the water molecule. A ZPE value of -4635.38 cm⁻¹ was obtained from 3D MCTDH calculations using the $V_{H_2O}(R_1, R_2, \gamma)$ potential of Eq. 1, that leads to a $E_0^{V^{6D}}$ energy of -1985.94 cm⁻¹. This ZPE value is very close to the

previously reported one of -1987.57 cm^{-1} ³⁹ from 6D calculations. Apart of some convergence errors, the difference of 1.63 cm^{-1} for the E_0 values should be also attributed to the exact kinetic energy operator employed here, instead of a rigid-rotor-like one used previously.³⁹

Figure 4: 3D plots of the $\text{H}_2\text{O}@\text{C}_{60}$ potential surface and the probability density distribution of the ground 0_{00} state in the XY-plane from the 6D calculations (see text).

In Fig. 4 we present the 3D probability distribution of the ground 0_{00} state obtained from the 6D calculations in the Cartesian XY-plane, together with the projection of the underlying potential energy surface. For the potential contour plots, the H_2O molecule is kept fixed at its equilibrium configuration with its center of mass moving in the XY-plane inside the C_{60} cage. Following, the ground state distribution probabilities obtained from the 9D calculations are shown in Fig. 5. The 2D (left panel) and 1D (right panel) probabilities are displayed in (R_1, R_2) and R/γ coordinates, respectively.

In Table 2 we also present the transition energies of the remaining 9 lowest states obtained for the BIR MCTDH calculations, their assignment, as well as comparisons with previous theoretical,³⁹ as well as experimental²⁶ data available. As in previous studies^{26,32} we labelled each state by three quantum numbers $J_{K_a K_c}$, where J is the total rotational angular momentum, while K_a and K_c are the angular momentum for prolate and oblate

Figure 5: Distribution probabilities of the internal water coordinates and the translational coordinates for the 0_{00} state from the 9D MCTDH calculations.

symmetric tops, respectively. We should note that para- H_2O states have total nuclear spin zero, and even parity for $K_a + K_c$, while for the ortho- H_2O states total nuclear spin is 1 and $K_a + K_c$ has odd parity. So, the 0_{00} and 1_{01} correspond to the ground vibrational state of the para- H_2O and ortho- H_2O , respectively. We also indexed the transitions as 1, 2, 3, and 4 corresponding to the INS and far-IR peaks of the experimental observations.²⁶ In Fig. 6 we show the molecular structure of the $\text{H}_2\text{O}@\text{C}_{60}$ and a level diagram representation of the lowest $J=0$ and 1 states together with the transitions determined by the INS and far-IR spectra.²⁶

For all the cases listed in Table 2 in this work we use the kinetic energy operator given in the supplementary material, that includes the full dimensional couplings of the system. One can see in Table 2, that for all energy values the inclusion of more degrees of freedom in the different approaches to the $\text{H}_2\text{O}@\text{C}_{60}$ potential (see Eqs. 4-7), does not produce relevant changes in the energy levels, with differences being less than 0.2 cm^{-1} between the values of the V^{6D} and V^{9D} potential forms. Moreover, the agreement is also very good for the rotationally excited energies reported in Table 2 and assigned to $J=1$ states. For the V^{6D} potential, the lowest 1_{01} , 1_{11} and 1_{10} levels are found, with respect to the 0_{00} state,

Figure 6: Schematic representation of $J = 0$ and $J = 1$ rotational levels for the $\text{H}_2\text{O}@\text{C}_{60}$ system. Also depicted with arrows, the transitions that give rise to the observed splittings (see text).

at 23.72 , 36.50 and 41.80 cm^{-1} , respectively, within 0.05 cm^{-1} with the previously reported 6D values.³⁹ Similarly values of 23.76 , 36.66 and 41.95 cm^{-1} are also obtained from the 9D MCTDH calculations, and the distribution probabilities of the ground ortho- H_2O ($1_{01}^{a,a',b}$) states in the (ϕ, θ, χ) rotational coordinates, from these calculations, are shown in Fig. 7.

One of the most interesting aspects of the experimental studies of the $\text{H}_2\text{O}@\text{C}_{60}$ system is loss of the degeneracy of the 1_{01} level that splits in two levels. This splitting has been experimentally measured and values of 4.8 ± 0.8 and $4.2 \pm 0.2 \text{ cm}^{-1}$ have been reported.^{26,32} Moreover, by analyzing the dependence of the INS spectra intensities as a function of temperature, it has been concluded³² that the ground ortho- H_2O state splits into the lowest two degenerated levels $1_{01}^{a,a'}$, and a higher energy level 1_{01}^b (see right panel of Fig. 6). As mentioned above, none of the previous and present 6D up to 9D calculations could predict any splitting of the ortho- H_2O state (see Fig. 6). However, as we discussed in subsection 2.2 recent studies on $\text{H}_2\text{O}@\text{C}_{60}$ interactions have concluded that the encaged H_2O molecule is not chemically isolated, with the presence of significant electronic interactions between H_2O and C_{60} cage, that seems to cause the elongation of the OH bonds.^{33–35,38} Further, another possible source of anisotropy could also be the presence of impurities in the external endofullerene environment.²⁵

Figure 7: Distribution probabilities for the 1_{01}^a (upper panels), $1_{01}^{a'}$ (middle panels), and 1_{01}^b (lower panels) states from the 9D MCTDH calculations.

Therefore, for studying the effect of such anisotropy that causes the symmetry breaking of the system we introduced the $\Delta V_{6D^{vib}}(R_v; R_1, R_2, \gamma, \phi, \theta, \chi)$ term (see Eq. 8) in the otherwise isotropic V^{6D} potential for the rigid C_{60} cage, that couples translational and vibrational motions in the $V_{R_v}^{9D^{vib}}$ n -mode form (see Eq. 8). We consider three different R_v values, corresponding to $R_v = 0.0$ bohr for water molecule at the center of mass of the fullerene

cage, and $R_v = 0.2$ and 0.4 bohr,

Figure 8: Potential plots and ground 0_{00} state along translational degrees of freedom: R coordinate (left panel) and α and β (right panels) from the 9D and $9D_{R_v=0.4}^{vib}$ MCTDH calculations.

In Fig. 8 we compared the probability density distributions along the R , α and β coordinates of the ground 0_{00} state from the 9D and $9D_{0.4}^{vib}$ calculations. One can see that no changes are found for the distributions in R , while as expected, uniform distributions for both α and β angles are obtained for the 9D case, while we observe some differences in those from the $9D_{0.4}^{vib}$ calculations. In Fig. 9 we present contour plots of the ground ortho- H_2O ($1_{01}^{a,a',b}$) state probabilities in (ϕ, θ, χ) rotational coordinates, obtained from the $9D_{0.4}^{vib}$ calculations. By comparing with those shown in Fig. 7, one can see some differences in the probability distributions of the states, mainly in the θ coordinate indicating a reorientation of the H_2O molecule inside the cage, similar to the configurations reported by first-principles electronic structure studies^{25,34,35,38} (see Fig. 4).

The splittings for all $J = 1$ states obtained from the all above mentioned 6D and 9DM-CTDH calculations, including also the results of previous theoretical and experimental studies available^{26,32,39–41} are listed in Table 3. One could see that for the V^{6D} , V^{9D} and $V_{0,0}^{9D^{vib}}$ potentials, the 1_{01} , 1_{11} and 1_{10} energies are within an accuracy of 0.1 cm^{-1} . However, for the $V_{0,2}^{9D^{vib}}$ and $V_{0,4}^{9D^{vib}}$ approaches, we obtained (see also Fig. 6) splittings of 0.49 and 1.90 cm^{-1} , respectively, with the degeneracy for the 1_{01} state being double for the lowest level and single for the highest one, in qualitative agreement with the experimental findings.³² Initially, the

Figure 9: Same as Fig. 7 from the $V_{0.4}^{9D^{vib}}$ MCTDH calculations.

comparison with previous studies should be made only with the V^{6D} calculations by Felker and Bačić,³⁹ that are referred to the same system using the same potential for describing the water- C_{60} interaction. However, we also summarized in Table 3 results from recent similar studies,^{40,41} assuming that the symmetry-breaking observed in the $H_2O@C_{60}$ solid phase. The authors have considered model cases, such as two $H_2O@C_{60}$ cages coupled by the electric dipole-dipole interaction between the water molecules,⁴⁰ and a fragment formed

by a central occupied C_{60} cage surrounded by twelve empty C_{60} molecules having different orientational orderings.⁴¹ The results of the dipole-dipole coupled model (V_{dd}^{6D}) have indicated splitting of the 1_{01} state only when the free water dipole moment values was used in the calculations.⁴⁰ In turn, the results of the fragment model⁴¹ have shown splitting of the 1_{01} level, that was very sensitive to the orientation of the empty C_{60} cages, as result of the quadrupolar interaction between them and the central one.

Further here, we also found that the 1_{11} and 1_{10} states are also splitted. The 1_{11} shows again a lowest level with degeneracy of 2 and a higher single degenerate state, with splittings of 0.21 and 0.90 cm^{-1} for the $V_{0.2}^{9D^{vib}}$ and $V_{0.4}^{9D^{vib}}$ forms, respectively. Contrary, for the first rotationally excited ortho- H_2O (1_{10}) level the highest state is double degenerated, with the lowest being single (see Fig. 6), with splittings of 0.65 cm^{-1} and 2.43 cm^{-1} for the $V_{0.2}^{9D^{vib}}$ and $V_{0.4}^{9D^{vib}}$ potential approaches, respectively.

Table 3: Splittings of the assigned rotational levels (in cm^{-1}) obtained from the MCTDH calculations using the indicated potential approaches (see Eqs. 4-8).^(a) From Ref.³⁹⁻⁴¹ ^(b) From Ref.^{26,32}

States	$V^{6D}/V_{dd}^{6D}/V_{ES}^{6D(a)}$	V^{6D}	V^{9D}	$V_{0.0}^{9D^{vib}}$	$V_{0.2}^{9D^{vib}}$	$V_{0.4}^{9D^{vib}}$	Expt. ^(b)
$1_{01}^{a,a'} \leftrightarrow 1_{01}^b$	0.0/1.14/4.25	0.03	0.03	0.02	0.49	1.90	$4.8 \pm 0.8 / 4.2 \pm 0.4$
$1_{11}^{a,a'} \leftrightarrow 1_{11}^b$	0.0/5.87/-	0.01	0.01	0.01	0.21	0.90	-
$1_{10}^b \leftrightarrow 1_{10}^{a,a'}$	-/2.93/-	0.07	0.07	0.05	0.65	2.43	-

We can see that the methodology used is capable of compute the experimental features given a potential approach that includes the possible source of system's anisotropy. However, the question raised is how realistic could be such anisotropy for considering the outcome predictions reliable, and what is the underlying source causing it? Here, we can only speculate that for the $H_2O@C_{60}$ endofullerene this could be mainly due to significant electronic noncovalent interactions between water molecule and cage. Recent electronic structure calculations have apparently demonstrated several conformations for the H_2O inside the cage, attributing the binding to the formation of $OH..C-C$ hydrogen bonds and weak $O...C$ contacts.^{34,35,38} Another although less possible source, external to the fullerene molecular environment, could

be the presence of impurities co-crystallized as $\text{H}_2\text{O}@\text{C}_{60}(\text{NiOEP})_2$,²⁵ that may also cause deformation and reorientation of the water molecule within the cage.

4 Summary and Conclusions

We derived a fully coupled (9D) hamiltonian that allows a complete description of a triatomic bent molecule embedded in a confined environment. We applied it to the $\text{H}_2\text{O}@\text{C}_{60}$ endofullerene within the MCTDH framework. We adapted a 7-mode combination scheme using a cluster expansion model of the 9D potential, that allows to study the anisotropy of the system in an incremental manner. By carrying out 6D reduced dimensional MCTDH calculations, we obtain an excellent agreement with previous reported results for the ground and $J = 1$ rotational excited states for $\text{H}_2\text{O}@\text{C}_{60}$ system. We have also investigated the low-lying $\text{H}_2\text{O}@\text{C}_{60}$ states from 9D MCTDH calculations. We have observed the experimental breaking of the degeneracy and the splitting of the 1_{01} by introducing a potential form that adds a source of anisotropy to the system. Our results indicate that the whole dimensionality of the system must be included in these kind of triatomic molecule-host system studies.

Regarding the splitting of the ground ortho- H_2O state, related with the origin of the symmetry breaking in the $\text{H}_2\text{O}@\text{C}_{60}$ endofullerene, we may speculate that arises from noncovalent inter-fullerene interactions or the presence of external impurities. The results presented here are obtained from an “exact” quantum mechanical treatment based on semiempirical potential forms. We found that the methodology developed is capable to reproduce the experimental features given an appropriate potential approach that includes such possible sources of system’s anisotropy. These calculations show the importance of a complete kinetic form for the description of the energetic landscape of these encapsulated systems, and encourage the computation of accurate *ab initio*-based potentials to fully described the anisotropies of the potential energy surface. The interaction of the guest molecule with its surroundings, and the accurate description of the molecular environment inside the cage are of critical im-

portance. Challenges now reside in the accurate description of the potential’s topology using first principles electronic structure approaches accounting both guest-cage and guest-lattice effects. The weak nature of such interactions is subject to surrounding effects, which may induce also specific behavior, and only by combining them with full-dimensional quantum treatments of the nuclear motions could lead to valuable results. Certainly, more efforts should be put in such rigorous and computationally demanding tasks. Work in this direction is in progress, to extend then at higher energy regimes for further comparison with experiments.

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Supporting Information Available

The Hamiltonian operator $\hat{H}$ expressed in the $\mathbf{q}=(R, \beta, \alpha, R_1, R_2, \gamma, \phi, \theta, \chi)$ coordinates is:

$$\begin{aligned} \hat{H} = & -\frac{\hbar^2}{2MR^2} \left[R^2 \frac{\partial^2}{\partial R^2} + \frac{\partial^2}{\partial \beta^2} + \cot(\beta) \frac{\partial}{\partial \beta} + \csc^2(\beta) \frac{\partial^2}{\partial \alpha^2} \right] \\ & -\frac{\hbar^2}{2\mu_1 R_1^2} \left[R_1^2 \frac{\partial^2}{\partial R_1^2} + 2R_1 \frac{\partial}{\partial R_1} + \frac{\partial^2}{\partial \gamma^2} + \cot(\gamma) \frac{\partial}{\partial \gamma} + \frac{\partial^2}{\partial \theta^2} + \cot(\theta) \frac{\partial}{\partial \theta} + \csc^2(\theta) \frac{\partial^2}{\partial \phi^2} \right. \\ & + (2 \cot(\gamma) \cot(\theta) \cos(\chi) + \cot^2(\gamma) + \cot^2(\theta)) \frac{\partial^2}{\partial \chi^2} + 2 \cot(\theta) \sin(\chi) \frac{\partial^2}{\partial \gamma \partial \chi} - 2 \csc(\theta) \sin(\chi) \frac{\partial^2}{\partial \phi \partial \gamma} \\ & + (-2 \cos(\chi) \cot(\gamma) \csc(\theta) - 2 \cot(\theta) \csc(\theta)) \frac{\partial^2}{\partial \phi \partial \chi} + 2 \cot(\gamma) \sin(\chi) \frac{\partial^2}{\partial \theta \partial \chi} - 2 \cos(\chi) \frac{\partial^2}{\partial \theta \partial \gamma} \left. \right] \\ & -\frac{\hbar^2}{2\mu_2 R_2^2} \left[R_2^2 \frac{\partial^2}{\partial R_2^2} + 2R_2 \frac{\partial}{\partial R_2} + \frac{\partial^2}{\partial \gamma^2} + \cot(\gamma) \frac{\partial}{\partial \gamma} + \csc^2(\gamma) \frac{\partial^2}{\partial \chi^2} \right] \\ & + \frac{\hbar^2}{m_O R_1 R_2} \left[\cos(\gamma) \frac{\partial^2}{\partial \gamma^2} - R_1 R_2 \cos(\gamma) \frac{\partial^2}{\partial R_1 \partial R_2} - \cos(\gamma) \cos(\chi) \frac{\partial^2}{\partial \theta \partial \gamma} \right. \\ & + R_1 \sin(\gamma) \frac{\partial^2}{\partial R_1 \partial \gamma} + R_2 \sin(\gamma) \frac{\partial^2}{\partial R_2 \partial \gamma} - R_2 \cos(\chi) \sin(\gamma) \frac{\partial^2}{\partial \theta \partial R_2} \\ & + \cos(\gamma) \cot(\theta) \sin(\chi) \frac{\partial^2}{\partial \gamma \partial \chi} + R_2 \cot(\theta) \sin(\gamma) \sin(\chi) \frac{\partial^2}{\partial R_2 \partial \chi} \\ & - R_2 \csc(\theta) \sin(\gamma) \sin(\chi) \frac{\partial^2}{\partial \phi \partial R_2} + \csc(\gamma) \sin(\chi) \frac{\partial^2}{\partial \theta \partial \chi} - \cos(\gamma) \csc(\theta) \sin(\chi) \frac{\partial^2}{\partial \phi \partial \gamma} \\ & + \csc(\gamma) \frac{\partial}{\partial \gamma} + \cot(\gamma) \csc(\gamma) \frac{\partial^2}{\partial \chi^2} + \cos(\chi) \cot(\theta) \csc(\gamma) \frac{\partial^2}{\partial \chi^2} - \cos(\chi) \csc(\gamma) \csc(\theta) \frac{\partial^2}{\partial \phi \partial \chi} \left. \right] + V(\mathbf{q}) \end{aligned}$$

m_O and m_H are the masses of the oxygen and hydrogen atoms, respectively. $M = m_O + 2m_H$ and μ_1 and μ_2 are the reduced masses $\mu_1 = \frac{m_O m_{H_1}}{m_O + m_{H_1}}$ and $\mu_2 = \frac{m_O m_{H_2}}{m_O + m_{H_2}}$.

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Graphical TOC Entry