Supporting Information

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SI Text

Ortho–Para Conversion Observed by Infrared Spectroscopy. Experimental data showing ortho-para conversion is given in Fig. S1.

Proton NMR Spectra. The proton MAS spectra in Fig. S3 indicate the presence of a protonated impurity in the sample, which gives rise to a strong NMR signal at room temperature. The proton density of the impurity is about 3 times that of the endohedral H_2O. However, the NMR signals from the impurity disappear at low temperature, in part because this signal becomes broader, and in part because this component exhibits a very long spin-lattice relaxation time. The endohedral proton signal remains narrow and these protons relax relatively rapidly, even at low temperature. At this time it is not known whether the impurity corresponds to a species included in the $H_2O@C_{60}$ matrix or whether it is a surface species.

Internuclear Dipole–Dipole Coupling in a Split Rotational Ground State. The vibrational and translational parts of the wave function are not relevant in the following discussion and will be neglected henceforth. The explicit forms of the rotational wave functions depend on the orientation of the molecular fixed frame M, as defined in the next paragraph, with respect to the laboratory reference frame L.

Assuming the water molecule to be rigid, with the position of the nuclei with respect to the nuclear center of mass given by the vectors r_o, r_{H_1} and r_{H_2} fixed in their equilibrium positions. The inertial tensor is given by

$$\mathbf{I} = \sum_q m_q(|\mathbf{r}_{q,i}|^2\delta_{i,j} - \mathbf{r}_{q,i}\mathbf{r}_{q,j}),$$

where the sum is over the three atomic nuclei. The principal axis system of the inertial tensor is defined as the system in which $\mathbf{I}$ is diagonal. Conventionally the three principal axes of the molecule are labeled by a, b, c so that the moments of inertia about the axes are in the order $I_{aa} < I_{bb} < I_{cc}$. Consequently the rigid rotor rotational Hamiltonian is given by (1)

$$\hat{H}_{\text{ROT}} = \frac{\hbar^2}{2I_{aa}}\hat{J}_a^2 + \frac{\hbar^2}{2I_{bb}}\hat{J}_b^2 + \frac{\hbar^2}{2I_{cc}}\hat{J}_c^2 = A\hat{J}_a^2 + B\hat{J}_b^2 + C\hat{J}_c^2 \quad \text{[S1]}$$

where are $\hat{J}_a, \hat{J}_b$ and $\hat{J}_c$ are the components of the angular momentum operator $\hat{\mathbf{J}}^2$ along the principal axes a, b, c and the rotational constants satisfy $A > B > C$. The axes of the molecular fixed frame M for rigid water are chosen to coincide with the principal axis system of the inertia tensor according to the following convention (1): the z axis is chosen to coincide with the a axis, and the x and y axes are along the b and c axes, respectively, so to form a right-handed system, see Fig. S2.

With such a choice of axes for the molecule fixed frame, the quantum wavefunctions for the three rotational sublevels of the *ortho* ground state 1_{01} are given by

$$\Phi_{m,0}^1(\Omega_{\text{LM}}) = \left(\frac{3}{8\pi^2}\right)^{1/2} D_{m,0}^1(\Omega_{\text{LM}})^*, \quad \text{[S2]}$$

with $m = -1, 0, 1$, see ref. 1 pp. 240–252, where $D_{m,k}^j$ are Wigner functions, the asterisk denotes the complex conjugate and $\Omega_{\text{LM}} = \{\phi, \theta, \chi\}$ are the Euler angles relating the molecular fixed frame to the laboratory frame. $\{\theta, \phi\}$ are the polar angles of the z axis in the laboratory frame and $\{\theta, \chi\}$ are the polar angles of the of the

Z axis of the laboratory frame in the molecular fixed frame. m represents the value of the projection of the angular momentum operator along the laboratory Z axis for the given wave function. In the icosahedral confinement of a rigid C_{60} cage the ground state of *ortho* water is three-fold degenerate in m.

Consider now the case in which the water molecule encounters an anisotropic local field, aligned with a local reference system, denoted A. The source of the local field is not important in the following discussion: it could be due to crystal packing effects, cage distortions, or mean electric dipolar fields from neighboring molecules. In all cases, the degeneracy on m is lifted by the presence of anisotropic local fields and the eigenfunctions describing the ground state of *ortho* water are given by:

$$\Psi_n(\Omega_{\text{LA}}, \Omega_{\text{LM}}) = \sum_{m=-1}^{1}\sum_{m'=-1}^{1}\Phi_{m,0}^1(\Omega_{\text{LM}})D_{m,m'}^1(\Omega_{\text{LA}})c_{m',n}$$

[S3]

for $n = -1, 0, 1$. Here $\Omega_{\text{LA}} = \{\alpha, \beta, \gamma\}$ represents the set of Euler angles determining the orientation of the local anisotropic field with respect to the laboratory. The coefficients $c_{m',n}$ depend on the local field Hamiltonian, but not on its orientation.

The dipolar interaction between two proton nuclear spins $\hat{I}_1$ and $\hat{I}_2$ is

$$H_{\text{DD}} = -\frac{\mu_0}{4\pi\,r_{\text{HH}}^3}\gamma^2\hbar^2[3(\hat{I}_1 \cdot \mathbf{e}_{\text{HH}})(\hat{I}_2 \cdot \mathbf{e}_{\text{HH}}) - \hat{I}_1 \cdot \hat{I}_2] \quad \text{[S4]}$$

where μ_0 is the vacuum permittivity, γ is the gyromagnetic factor for protons, $\hbar$ is the reduced Planck constant, r_{HH} is the distance between the two protons (assumed to be constant), and $\mathbf{e}_{\text{HH}}$ denotes a unit vector along the line joining the two protons. The spherical form of the dipolar Hamiltonian is (2)

$$H_{\text{DD}}(\Omega_{\text{LP}}) = \sqrt{6}\omega_{\text{HH}}^{\text{loc}}\sum_{p=-2}^{2}(-1)^p D_{p,0}^2(\Omega_{\text{LP}})^* T_{-p}^2(\hat{\mathbf{I}}_1, \hat{\mathbf{I}}_2) \quad \text{[S5]}$$

where $\omega_{\text{HH}}^{\text{loc}} = -\mu_0\gamma^2\hbar^2/4\pi r_{\text{HH}}^3$ is the dipolar coupling for localized protons. From the equilibrium configuration of the water molecule, shown in Fig. S2, $r_{\text{HH}} = 1.515$ Å and $\omega_{\text{HH}}^{\text{loc}}/2\pi\hbar = -34.5$ kHz. $T_p^2(\hat{\mathbf{I}}_1, \hat{\mathbf{I}}_2)$ are the spherical tensor operators of rank 2 and component p in the proton spin operators:

$$T_0^2(\hat{\mathbf{I}}_1, \hat{\mathbf{I}}_2) = \frac{1}{\sqrt{6}}(3\hat{I}_{1,z}\hat{I}_{2,z} - \hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_1)$$

$$T_{\pm 1}^2(\hat{\mathbf{I}}_1, \hat{\mathbf{I}}_1) = \mp\frac{1}{2}(\hat{I}_{1,z}\hat{I}_{2,\pm} + \hat{I}_{1,\pm}\hat{I}_{2,z}) \quad \text{[S6]}$$

$$T_{\pm 2}^2(\hat{I}_1, \hat{I}_2) = \frac{1}{2}\hat{I}_{1,\pm}\hat{I}_{2,\pm}$$

with $\hat{I}_{s,\pm} = \hat{I}_{s,x} \pm i\hat{I}_{s,y}, s = 1, 2$. Ω_{LP} is the set of Euler angles determining the orientation of the principal axis frame P of the dipolar Hamiltonian, defined to have its z' axis along the internuclear H–H vector, with respect to the laboratory frame L. The notation $H_{\text{DD}}(\Omega_{\text{LP}})$ in Eq. **5** stresses the dependence of the dipolar Hamiltonian on the orientation of the molecule in the laboratory frame. We note that with the choice of the axes given above for the molecular fixed frame P coincides M and then $\Omega_{\text{LP}} = \Omega_{\text{LM}}$.

In high static magnetic field the nuclear Zeeman interaction $H_Z = -\gamma \boldsymbol{B}_0 \cdot (\hat{\boldsymbol{I}}_1 + \hat{\boldsymbol{I}}_2)$ is dominating over all the other spin interaction. The NMR lineshape is determined by the part of $H_{DD}(\Omega_{LP})$ which commutes with H_Z. By choosing the Z axis of the laboratory frame to be aligned along the magnetic field, the truncated dipolar Hamiltonian is

$$H_{DD}^0(\Omega_{LM}) = \sqrt{6}\omega_{HH}^{loc} D_{0,0}^2(\Omega_{LM})^* T_0^2(\hat{\boldsymbol{I}}_1, \hat{\boldsymbol{I}}_2)$$
$$= \sqrt{6}\omega_{HH}^{loc} \frac{1}{2}(3\cos^2\theta - 1) T_0^2(\hat{\boldsymbol{I}}_1, \hat{\boldsymbol{I}}_2) \quad \textbf{[S7]}$$

$H_{DD}^0(\Omega_{LM})$ is the truncated dipolar Hamiltonian for a localized water molecule fixed in a given orientation with respect to the external magnetic field.

In the *ortho*-$H_2O@C_{60}$ ground state the truncated dipolar Hamiltonian is given by the quantum and thermal average of dipolar Hamiltonian (3, 4)

$$\bar{H}_{DD}^0(\Omega_{LA}) = \sum_{n=-1}^{1} \langle \Psi_n(\Omega_{LA}, \Omega_{LM}) | H_{DD}^0(\Omega_{LM}) |$$
$$\Psi_n(\Omega_{LA}, \Omega_{LM}) \rangle p_n(T)$$
$$= \sqrt{6}\omega_{HH}^{loc} \sum_{n=-1}^{1} \langle \Psi_n(\Omega_{LA}, \Omega_{LM}) | D_{0,0}^2(\Omega_{LM})^* |$$
$$\Psi_n(\Omega_{LA}, \Omega_{LM}) \rangle p_n(T) T_0^2(\hat{\boldsymbol{I}}_1, \hat{\boldsymbol{I}})$$
$$= \sqrt{6}\frac{\omega_{HH}^{loc}}{5} \sum_{n=-1}^{1} \sum_{m=-1}^{1} \sum_{m'=-1}^{1} (2 - 3m^2)$$
$$|D_{m,m'}^1(\Omega_{LA}) c_{m',n}|^2 p_n(T) T_0^2(\hat{\boldsymbol{I}}_1, \hat{\boldsymbol{I}}_2) \quad \textbf{[S8]}$$

where $p_n(T)$ is the Boltzmann population of the sublevel n. The local field defines the quantization frame for the effective Hamiltonian. The presence of spinning sidebands in the magic angle

spinning NMR spectrum of $H_2O@C_{60}$ is directly related to anisotropic fields in the solid state lifting the degeneracy of the rotational sublevels. No sidebands are expected in an icosahedral confinement where the choice of the frame A is arbitrary. In such a case $c_{m',n} = \delta_{m',n}$, $p_n(T) = 1/3$, $\sum_{m'=-1}^{1} |D_{m,m'}^1(\Omega_{LA})|^2 = 1$ and $\bar{H}_{DD}^0(\Omega_{LA}) = 0$. In the case of an axially symmetric local field the *ortho* ground state splits into one longitudinal polarized state ($n = 0$) and two degenerate transverse polarized states ($n = \pm 1$), separated by an energy gap ΔE, and with coefficients satisfying $c_{m',n} = \delta_{m',n}$. The effective dipolar Hamiltonian reduces to

$$\bar{H}_{DD}^0(\Omega_{LA}) = \sqrt{6}\left(-\frac{2}{5}\omega_{DD}\frac{1 - e^{-\Delta E/k_B T}}{1 + 2e^{-\Delta E/k_B T}}\right)$$
$$\times \left(\frac{3\cos^2\beta - 1}{2}\right) T_0^2(\hat{\boldsymbol{I}}_1, \hat{\boldsymbol{I}}_2) \quad \textbf{[S9]}$$

The proton NMR lineshape is the same as expected for two localized protons, compare to Eq. **5**, but with an effective dipolar constant given by

$$\omega_{HH}^{eff}(T) = -\frac{2}{5}\omega_{HH}^{loc}\frac{1 - e^{-\Delta E/k_B T}}{1 + 2e^{-\Delta E/k_B T}} \quad \textbf{[S10]}$$

The experimental value of −5.5 kHz, obtained from the magic angle spinning solid state NMR of $H_2O@C_{60}$ at 9.6 K, is then consistent with an energy gap of 0.9 meV.

We note that the factor of (2/5), which arises from the quantum delocalization of the *ortho*-water rotational wavefunctions, has sometimes been overlooked in the literature. An example of this kind is found in ref. 5, in which the factor (2/5) was omitted, leading to erroneous conclusions to be drawn over the distorted geometry of water molecules in gas-phase complexes, observed by microwave spectroscopy.

1. Bunker PR, Jensen P (2006) *Molecular Symmetry and Spectroscopy* (NRC Research Press, Ottawa).
2. Mehring M (1982) *High Resolution NMR in Solids* (Springer, Berlin) 2nd Ed.
3. Carravetta M, et al. (2007) Solid-state NMR of endohedral hydrogen-fullerene complexes. *Phys Chem Chem Phys* 9:4879–4894.
4. Hall RT, Dowling JM (1967) Pure rotational spectrum of water vapor. *J Chem Phys* 47:2454–2461.
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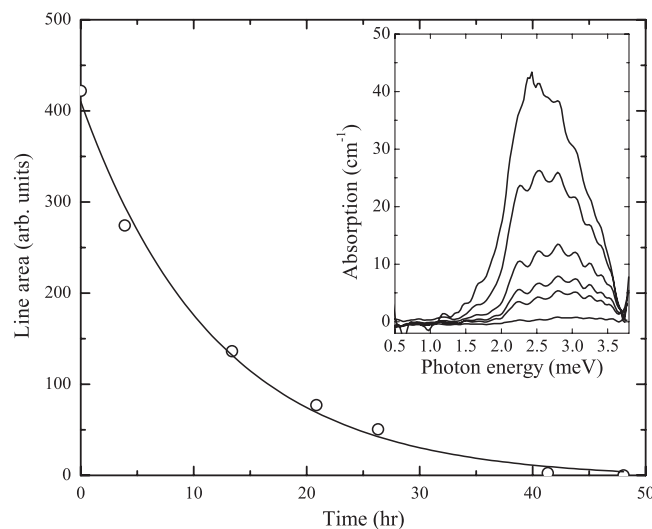
Fig. S1. Time dependence of the area of line "3" (circles) measured at 3.5 K after cool down from 77 K. The spectrum, measured at 48 h (see Fig. 3) was subtracted before integration and the line area was obtained by integrating difference spectra, shown in the inset, from 1.1 meV to 3.7 meV. The intensity of line "3," which is the ortho transition (Fig. 1), decreases in time because of ortho to para conversion. Solid line is a single exponential fit, tau = (12.0 ± 1.3) h.
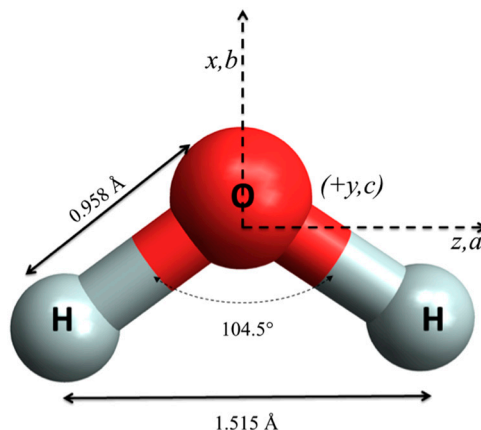
Fig. S2. Equilibrium geometry of a free water molecule. The molecular fixed frame *xyz* is defined such that the inertial tensor is diagonal. This paper follows the convention of ref. 1, in which the inertial eigenvalues are ordered such that $I_{aa} < I_{bb} < I_{cc}$ and the $\{x, y, z\}$ axes are identified with the *(8)* eigenvalues, respectively. With this convention the *z*-axis is parallel to the vector joining the two protons and the molecule lies in the *xz*-plane.
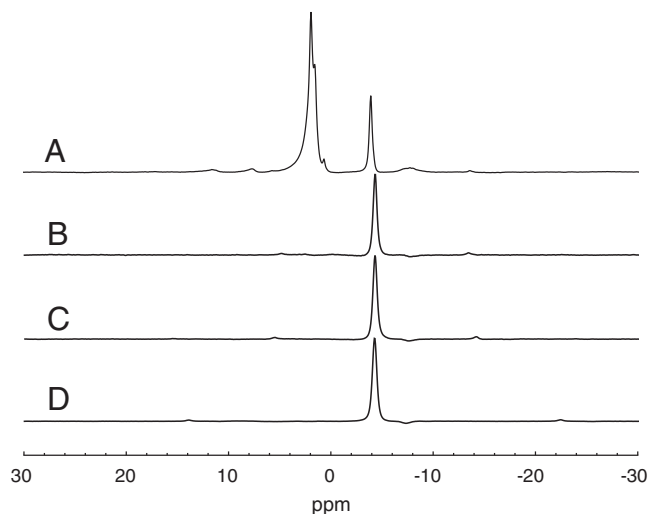

Fig. S3. Magic-angle-spinning proton NMR spectra of $H_2O@C_{60}$, taken in a magnetic field of 14.1 T (proton precession frequency ≈ -600.0 MHz). All spectra were obtained by taking the Fourier transform of a single transient after a 90° excitation pulse and subjecting it to Lorentzian linebroadening with a linewidth of 200 Hz followed by baseline correction. The sample temperatures and spinning frequencies are (*A*) 293.0 K, 5.80 kHz; (*B*) 138.0 K, 5.44 kHz; (*C*) 83.0 K, 5.82 kHz; (*D*) 41 K, 10.83 kHz. The peak at −4.6 ppm are from the protons of the endohedral water. The full-width-at-half-height of the endohedral proton peak is about 200 Hz before Lorentzian broadening. The peak at 1.8 ppm in spectrum A is from a protonated impurity. At room temperature the impurity signal has an integrated area of 3:1 with respect to that of the endohedral peak. The impurity peak disappears at low temperatures due to a combination of broadening effects and exceedingly long T_1.