Supplementary Information to 'Interactions between water and C_{60} in the endohedral fullerene $H_2O@C_{60}$'

1 Relations between coordinate systems

The coordinates of a point in the molecule-fixed coordinate system $\{x_w, y_w, z_w\}$ are related to coordinates in a space-fixed system $\{x, y, z\}$ with the same origin by[1]

$$\begin{pmatrix} x_w \\ y_w \\ z_w \end{pmatrix} = A(\phi,\theta,\chi) \begin{pmatrix} x \\ y \\ z \end{pmatrix} \tag{1}$$

where $A(\phi,\theta,\chi)$ is the product of three Euler rotation matrices

$$A(\phi,\theta,\chi) = \begin{pmatrix} \cos\chi & \sin\chi & 0 \\ -\sin\chi & \cos\chi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \cos\theta & 0 & -\sin\theta \\ 0 & 1 & 0 \\ \sin\theta & 0 & \cos\theta \end{pmatrix} \begin{pmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{2}$$

Coordinates in a space-fixed system with origin at the centre of a C_{60} molecule are therefore

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x_{\mathrm{cm}} \\ y_{\mathrm{cm}} \\ z_{\mathrm{cm}} \end{pmatrix} + A^{-1}(\phi,\theta,\chi) \begin{pmatrix} x_w \\ y_w \\ z_w \end{pmatrix} \tag{3}$$

where $\{x_{\mathrm{cm}}, y_{\mathrm{cm}}, z_{\mathrm{cm}}\} = R_{\mathrm{cm}}\{\sin\theta_{\mathrm{cm}}\cos\phi_{\mathrm{cm}}, \sin\theta_{\mathrm{cm}}\sin\phi_{\mathrm{cm}}, \cos\theta_{\mathrm{cm}}\}$ is the position of the centre of mass of the water molecule relative to the centre of the C_{60} molecule expressed in spherical polar coordinates $\{R_{\mathrm{cm}}, \theta_{\mathrm{cm}}, \phi_{\mathrm{cm}}\}$.

2 Rotational basis states and angular momentum

The rotational states are written in terms of complex conjugates of Wigner matrices $D^{(j)}_{m,k}(\phi,\theta,\chi)$ involving the Euler angles $\{\phi,\theta,\chi\}$. We use the definition[1]

$$\begin{aligned} D^{(j)*}_{m,k}(\phi,\theta,\chi) &= \sqrt{(j+m)!(j-m)!(j+k)!(j-k)!}\times \\ & \sum_{\sigma=\max(0,k-m)}^{\min(j-m,j+k} \frac{(-1)^\sigma \left(\cos\frac{\theta}{2}\right)^{2j+k-m-2\sigma} \left(-\sin\frac{\theta}{2}\right)^{m-k+2\sigma} \mathrm{e}^{\mathrm{i}m\phi}\mathrm{e}^{\mathrm{i}k\chi}}{\sigma!(j-m-\sigma)!(m-k+\sigma)!(j+k-\sigma)!}. \end{aligned} \tag{4}$$

As Wigner matrices are related to their complex conjugates by $D^{(j)}_{m,k} = (-1)^{m-k} D^{(j)*}_{-m,-k}$, the rotational states can also be defined in terms of Wigner matrices directly rather than their complex conjugates.

The components of the rotational angular momentum with respect to the molecule-fixed axes $\{x_w, y_w, z_w\}$ can be written in terms of derivatives of the Euler angles as[1]

$$\begin{aligned} \hat{J}_{x_w} &= -\mathrm{i}\left(\sin\chi\frac{\partial}{\partial\theta} - \csc\theta\cos\chi\frac{\partial}{\partial\phi} + \cot\theta\cos\chi\frac{\partial}{\partial\chi}\right) \\ \hat{J}_{y_w} &= -\mathrm{i}\left(\cos\chi\frac{\partial}{\partial\theta} + \csc\theta\sin\chi\frac{\partial}{\partial\phi} - \cot\theta\sin\chi\frac{\partial}{\partial\chi}\right) \\ \hat{J}_{z_w} &= -\mathrm{i}\frac{\partial}{\partial\chi} \end{aligned} \tag{5}$$

3 Properties of Wigner matrices and spherical harmonics

In order to obtain analytical expressions for the matrix elements of the perturbation V between rotational basis states, we use the relation that allows the product of two Wigner matrices to be written in terms of a sum of single Wigner matrices (Equation (11) in the main text) combined with the orthogonality relations

$$\int_0^{2\pi}\int_0^{\pi}\int_0^{2\pi} D^{(j')}_{m',k'}(\phi,\theta,\chi)D^{(j)}_{m,k}(\phi,\theta,\chi)\sin\theta\, d\chi\, d\theta\, d\phi = \frac{8\pi^2}{2j+1}\delta_{m',m}\delta_{k',k}\delta_{j',j} \tag{6}$$

where the $\delta_{m',m}$ are Kronecker delta functions. To evaluate matrix elements between translational states, we use the integral

$$\begin{aligned}\int_0^{2\pi}\int_0^{\pi} & Y_{l_1,m_1}(\theta_{\rm cm},\phi_{\rm cm})Y_{l_2,m_2}(\theta_{\rm cm},\phi_{\rm cm})Y_{l_3,m_3}(\theta_{\rm cm},\phi_{\rm cm})\sin\theta_{\rm cm}\, d\theta_{\rm cm}\, d\phi_{\rm cm} \\ &= \sqrt{\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}}\begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3\end{pmatrix}\end{aligned} \tag{7}$$

where the $\begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3\end{pmatrix}$ are Wigner $3j$-symbols.

4 Additional $A_g^{(s)}$ states in $S_6^{(12)}$ symmetry

Table 3 in the main text shows states up to $l = 2$ and $J = 2$ that were derived for $S_6^{(12)}$ symmetry but which actually have spherical or spheroidal symmetry. There are 17 additional $A_g^{(s)}$ states up to $l = 2$ and $J = 2$ that do have a lower symmetry. Of these, 5 occur when our calculations are repeated for $D_{3d}^{(12)}$ symmetry. The remaining 12 only occur in $S_6^{(12)}$ symmetry. The results are shown below where, as in the main text, normalised states ψ_{i,N_r} are obtained by dividing the results in this table by 4π.

Symmetry	l	J	$4\pi\psi^{(s)}_{A_{1g}} \equiv 4\pi\psi_{i,N_r}$
$D_{3d}^{(12)}$	1	2	$\sqrt{\frac{5}{2}}\left(D^{(2)-}_{2,2}Y_{1,-1} + D^{(2)-}_{-2,2}Y_{1,1}\right)\phi_{N_r,1}$
	2	2	$\sqrt{5}\left(D^{(2)}_{1,0}Y_{2,-2} - D^{(2)}_{-1,0}Y_{2,2}\right)\phi_{N_r,2}$
	2	2	$\sqrt{\frac{5}{2}}\left(D^{(2)+}_{1,2}Y_{2,-2} - D^{(2)+}_{-1,2}Y_{2,2}\right)\phi_{N_r,2}$
	2	2	$\sqrt{5}\left(D^{(2)}_{2,0}Y_{2,-1} - D^{(2)}_{-2,0}Y_{2,1}\right)\phi_{N_r,2}$
	2	2	$\sqrt{\frac{5}{2}}\left(D^{(2)+}_{2,2}Y_{2,-1} - D^{(2)+}_{-2,2}Y_{2,1}\right)\phi_{N_r,2}$
$S_6^{(12)}$	1	1	$\sqrt{3}\left(D^{(1)}_{-1,0}Y_{1,-1} - D^{(1)}_{1,0}Y_{1,1}\right)\phi_{N_r,1}$
	1	2	$\sqrt{\frac{5}{2}}\left(D^{(2)-}_{2,2}Y_{1,-1} - D^{(2)-}_{-2,2}Y_{1,1}\right)\phi_{N_r,1}$
	1	2	$\sqrt{\frac{5}{2}}\left(D^{(2)-}_{-1,2}Y_{1,-1} + D^{(2)-}_{1,2}Y_{1,1}\right)\phi_{N_r,1}$
	1	2	$\sqrt{5}D^{(2)-}_{0,2}Y_{1,0}\phi_{N_r,1}$
	2	2	$\sqrt{5}\left(D^{(2)}_{-1,0}Y_{2,-1} - D^{(2)}_{1,0}Y_{2,1}\right)\phi_{N_r,2}$
	2	2	$\sqrt{\frac{5}{2}}\left(D^{(2)+}_{-1,2}Y_{2,-1} - D^{(2)+}_{1,2}Y_{2,1}\right)\phi_{N_r,2}$
	2	2	$\sqrt{5}\left(D^{(2)}_{-2,0}Y_{2,-2} - D^{(2)}_{2,0}Y_{2,2}\right)\phi_{N_r,2}$
	2	2	$\sqrt{\frac{5}{2}}\left(D^{(2)+}_{-2,2}Y_{2,-2} - D^{(2)+}_{2,2}Y_{2,2}\right)\phi_{N_r,2}$
	2	2	$\sqrt{\frac{5}{2}}\left(D^{(2)+}_{2,2}Y_{2,-1} + D^{(2)+}_{-2,2}Y_{2,1}\right)\phi_{N_r,2}$
	2	2	$\sqrt{5}\left(D^{(2)}_{2,0}Y_{2,-1} + D^{(2)}_{-2,0}Y_{2,1}\right)\phi_{N_r,2}$
	2	2	$\sqrt{\frac{5}{2}}\left(D^{(2)+}_{1,2}Y_{2,-2} + D^{(2)+}_{-1,2}Y_{2,2}\right)\phi_{N_r,2}$
	2	2	$\sqrt{5}\left(D^{(2)}_{1,0}Y_{2,-2} + D^{(2)}_{-1,0}Y_{2,2}\right)\phi_{N_r,2}$

References

[1] P. R. Bunker and P. Jensen, *Fundamentals of Molecular Symmetry*, IOP Publishing, Bristol, 2005.