Supplementary Information for: Effects of symmetry breaking on the translation-rotation eigenstates of \( \text{H}_2 \), HF, and \( \text{H}_2\text{O} \) inside the fullerene \( \text{C}_{60} \)

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1 Hamiltonian Parameters

1.1 \( \text{H}_2@\text{C}_{60} \)

The kinetic energy operator for \( \text{H}_2@\text{C}_{60} \) was taken to be

\[
\hat{T} = -\frac{\nabla^2}{2M} + B\hat{j}^2
\]

(1)

where \( \nabla^2 \) is the Laplacian associated with \( \mathbf{R} \), \( \hat{j}^2 \) is the operator corresponding to the square of the rotational angular momentum of the \( \text{H}_2 \), \( M \) is the mass of the \( \text{H}_2 \), and \( B \) is the
rotational constant of the H$_2$. We used $M = 2.0104$ amu, $B = 58.378$ cm$^{-1}$ for the $v = 0$ manifold, and $B = 54.83$ cm$^{-1}$ for the $v = 1$ manifold.

The $V_{M-C_{60}}$ function for both the $v = 0$ and the $v = 1$ manifolds was taken to be a pairwise-additive Lennard-Jones one of the form

$$V_{H_2-C_{60}} = \sum_{i=1}^{3} \sum_{k=1}^{60} 4w_i\epsilon \left[ \left( \frac{\sigma}{r_{ik}} \right)^{12} - \left( \frac{\sigma}{r_{ik}} \right)^6 \right],$$

where $i$ runs over three H$_2$ sites, $k$ runs over the 60 nuclear positions of the C atoms in the central cage, and $r_{ik}$ is the distance between site $i$ and site $k$. For both manifolds the H$_2$ site 1 was located at the center of the HH bond, and sites 2 and 3 were located at the H nuclei. For $v = 0$ the HH bond distance was taken to be 0.74 Å, $w_1 = 6.7$, $w_2 = w_3 = 1$, $\sigma = 2.95$ Å, and $\epsilon = 3.07$ cm$^{-1}$.\textsuperscript{1} For $v = 1$ the HH bond distance was taken to be 0.78132 Å, $w_1 = 7.5$, $w_2 = w_3 = 1$, $\sigma = 2.95$ Å, and $\epsilon = 2.9886668$ cm$^{-1}$.\textsuperscript{2} The C$_{60}$ geometry was taken to be that used in Felker, et al.\textsuperscript{3}

As to $V_{\text{quad}}$, the BF $\hat{z}$ axis was taken to be the internuclear axis, and the one nonzero BF quadrupole component for H$_2$ was taken to be $Q_0^{\text{BF}} = 0.499$ au for both the $v = 0$ and $v = 1$ manifolds. This is the same value that was used in Felker, et al.\textsuperscript{3}

### 1.2 HF@C$_{60}$

The kinetic energy operator for HF@C$_{60}$ was taken to have the same form as eqn (1) but with $M = 20.006225$ amu and $B = 18.523$ cm$^{-1}$. This value for $B$ is the cage-modified one determined by Kalugina and Roy.\textsuperscript{4}

The $V_{HF-C_{60}}$ function was taken directly from Kalugina and Roy.\textsuperscript{4} It is an expansion over bipolar spherical tensors dependent on the four angles $(\Theta, \Phi, \omega)$ with $R$-dependent expansion coefficients. It does not require any input as to the C$_{60}$ geometry.

The BF $\hat{z}$ axis was taken by Kalugina and Roy\textsuperscript{5} to be the internuclear axis pointing from the H nucleus to the F nucleus. As such $\vec{\mu} = \mu \hat{z}$ is antiparallel to $\hat{z}$ and $\mu$ is negative. We
take the magnitude of $\mu$ to be the screened value of $-0.177$ au from Krachmalnicoff, et al.\(^6\)

1.3 $\text{H}_2\text{O}@\text{C}_{60}$

The kinetic energy operator for $\text{H}_2\text{O}@\text{C}_{60}$ was taken to be

$$\hat{T} = -\nabla^2 \frac{1}{2M} + B_x \hat{j}_x^2 + B_y \hat{j}_y^2 + B_z \hat{j}_z^2 \quad (3)$$

where $\nabla^2$ is the Laplacian associated with $\mathbf{R}$, $\hat{j}_x$, $\hat{j}_y$, and $\hat{j}_z$ are the operators associated with the components of the rotational angular momentum of the $\text{H}_2\text{O}$ along the BF axes, which are taken to be its principal inertial axes. We used $M = 18.0105$ amu, $B_x = 27.877$ cm\(^{-1}\), $B_y = 9.285$ cm\(^{-1}\), and $B_z = 14.512$ cm\(^{-1}\). This choice of the BF axes locates the bisector of the HOH bond angle to be along the BF $\hat{z}$ axis.

The $V_{M-\text{C}_{60}}$ for $\text{H}_2\text{O}@\text{C}_{60}$ was taken from Felker and Bačič\(^7\) and is given by

$$V_{\text{H}_2\text{O}-\text{C}_{60}} = \sum_{i=1}^{3} \sum_{k=1}^{60} 4\epsilon_i \left[ \left( \frac{\sigma_i}{r_{ik}} \right)^{12} - \left( \frac{\sigma_i}{r_{ik}} \right)^6 \right], \quad (4)$$

where $i$ runs over three $\text{H}_2\text{O}$ sites, $k$ runs over the 60 nuclear positions of the C atoms in the central cage, $r_{ik}$ is the distance between site $i$ and site $k$, $\sigma_1 = 3.372$ Å, $\sigma_2 = \sigma_3 = 2.640$ Å, $\epsilon_1 = 36.34$ cm\(^{-1}\), and $\epsilon_2 = \epsilon_3 = 8.95384$ cm\(^{-1}\). The three $\text{H}_2\text{O}$ sites are given in Table 2 of the ESI of Felker, et al.\(^3\) The $\text{C}_{60}$ geometry was taken to be the same as that used for $\text{H}_2@\text{C}_{60}$.

As to $V_{\text{quad}}$, since we take the BF $\hat{z}$ axis to point from the c.m. of the water moiety toward the O nucleus along the HOH bond-angle bisector, then $\vec{\mu} = \mu \hat{z}$ is antiparallel to $\hat{z}$, and $\mu$ is negative. We used the screened dipole value, $\mu = -0.200$ au, from Goh, et al.\(^8\) The BF quadrupole components of the $\text{H}_2\text{O}$ were taken to be the same as in Felker, et al.:\(^3\) $Q_0^{(BF)} = -0.09973$ au and $Q_{\pm 2}^{(BF)} = 1.53843$ au.
2 Grid Parameters

As mentioned in Subsection 2.2 of the main body of the paper the TR state function, $|\psi\rangle$, employed in the Chebyshev filter diagonalization procedure was transformed to a grid representation to effect its multiplication by the potential-energy portion of $\hat{H}$. The general nature of the five-dimensional (5D) grid points used for H$_2@C_{60}$ and for HF@C$_{60}$, and the six-dimensional (6D) grid points used for H$_2$O@C$_{60}$ are described in Section 2.5 of Felker, et al. Further specifics as to the grids used in this work follow.

For $M$=H$_2$ we used (i) 12 Gauss-associated-Laguerre quadrature points generated as per Felker and Bačić with $\beta = 2.9888989$ au for the $R$ coordinate, (ii) 10 Gauss-Legendre quadrature points for the $\cos \Theta$ coordinate, (iii) 18 Fourier grid points for the $\Phi$ coordinate, (iv) 10 Gauss-Legendre quadrature points for the $\cos \theta$ coordinate, and (v) 18 Fourier grid points for the $\phi$ coordinate. Here, the relevant Euler angles are $\omega = (\theta, \phi)$, where $\theta$ is the polar angle, and $\phi$ the azimuthal angle describing the orientation of the BF $\hat{z}$ axis with respect to the SF axis system.

For $M$=HF we used (i) 14 Gauss-associated-Laguerre quadrature points generated with $\beta = 12.0$ au for the $R$ coordinate, (ii) 12 Gauss-Legendre quadrature points for the $\cos \Theta$ coordinate, (iii) 24 Fourier grid points for the $\Phi$ coordinate, (iv) 10 Gauss-Legendre quadrature points for the $\cos \theta$ coordinate, and (v) 18 Fourier grid points for the $\phi$ coordinate.

For $M$=H$_2$O we used (i) 12 Gauss-associated-Laguerre quadrature points generated with $\beta = 24.38$ au for the $R$ coordinate, (ii) 10 Gauss-Legendre quadrature points for the $\cos \Theta$ coordinate, (iii) 18 Fourier grid points for the $\Phi$ coordinate, (iv) 10 Gauss-Legendre quadrature points for the $\cos \theta$ coordinate, (v) 18 Fourier grid points for the $\phi$ coordinate, and (vi) 18 Fourier grid points for the $\chi$ coordinate. Here, $\omega = (\phi, \theta, \chi)$ are the Euler angles, defined with the convention used in Zare, that specify the orientation of the BF axes of the H$_2$O with respect to the SF axes.
References


(5) P. N. Roy, private communication.


