Supplementary Information for: Effects of symmetry breaking on the translation-rotation eigenstates of H_2, HF, and H_2O inside the fullerene C_{60}[†]

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1 Hamiltonian Parameters

1.1 $H_2@C_{60}$

The kinetic energy operator for $H_2@C_{60}$ was taken to be

$$\hat{T} = -\frac{\nabla^2}{2M} + B\hat{j}^2 \tag{1}$$

where ∇^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 H_2, M is the mass of the 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

$$V_{H_2-C_{60}} = \sum_{i=1}^{3} \sum_{k=1}^{60} 4 w_i \epsilon \left[\left(\frac{\sigma}{r_{ik}} \right)^{12} - \left(\frac{\sigma}{r_{ik}} \right)^{6} \right], \tag{2}$$

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}.[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}.[2] The C_{60} geometry was taken to be that used in Felker, et al.[3]

As to V_{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.[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.[4]

The $V_{HF-C_{60}}$ function was taken directly from Kalugina and Roy.[4] It is an expansion over bipolar spherical tensors dependent on the four angles (Θ, Φ, ω) 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[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 μ is negative. We take the magnitude of μ to be the screened value of -0.177 au from Krachmalnicoff, et al.[6]

1.3 $H_2O@C_{60}$

The kinetic energy operator for $H_2O@C_{60}$ was taken to be

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

where ∇^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 H_2O along the BF axes, which are take 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 $V_{M-C_{60}}$ for $H_2O@C_{60}$ was taken from Felker and Bačić[7] and is given by

$$V_{H_2O-C_{60}} = \sum_{i=1}^{3}\sum_{k=1}^{60} 4\epsilon_i\left[\left(\frac{\sigma_i}{r_{ik}}\right)^{12} - \left(\frac{\sigma_i}{r_{ik}}\right)^{6}\right], \tag{4}$$

where i runs over three H_2O 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 H_2O sites are given in Table 2 of the ESI of Felker, et al.[3] The C_{60} geometry was taken to be the same as that used for $H_2@C_{60}$.

As to V_{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 μ is negative. We used the screened dipole value, $\mu = -0.200$ au, from Goh, et al.[8] The BF quadrupole components of the H_2O were taken to be the same as in Felker, et al.:[3] $Q_0^{(\text{BF})} = -0.09973$ au and $Q_{\pm 2}^{(\text{BF})} = 1.53843$ 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 $H_2O@C_{60}$ are described in Section 2.5 of Felker, et al.[3] 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[9] 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 Φ coordinate, (iv) 10 Gauss-Legendre quadrature points for the $\cos\theta$ coordinate, and (v) 18 Fourier grid points for the ϕ coordinate. Here, the relevant Euler angles are $\omega = (\theta, \phi)$, where θ is the polar angle, and ϕ 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 Φ coordinate, (iv) 10 Gauss-Legendre quadrature points for the $\cos\theta$ coordinate, and (v) 18 Fourier grid points for the ϕ coordinate.

For M=H_2O 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 Φ coordinate, (iv) 10 Gauss-Legendre quadrature points for the $\cos\theta$ coordinate, (v) 18 Fourier grid points for the ϕ coordinate, and (vi) 18 Fourier grid points for the χ coordinate. Here, $\omega = (\phi, \theta, \chi)$ are the Euler angles, defined with the convention used in Zare,[10] that specify the orientation of the BF axes of the H_2O with respect to the SF axes.

References

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