Supplementary Information for: Explaining the symmetry breaking observed in the endofullerenes $H_2@C_{60}$, HF@C_{60}, and $H_2O@C_{60}$

Peter M. Felker,*,† Vojtěch Vlček,† Isaac Hietanen,‡ Stephen FitzGerald,‡ Daniel Neuhauser,† and Zlatko Bačić*,¶,§

†*Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095-1569, USA*

‡*Department of Physics and Astronomy, Oberlin College, Oberlin, Ohio 44074, USA*

¶*Department of Chemistry, New York University, New York, New York 10003, USA*

§*NYU-ECNU Center for Computational Chemistry at NYU Shanghai, 3663 Zhongshan Road North, Shanghai 200062, China*

E-mail: felker@chem.ucla.edu; zlatko.bacic@nyu.edu

1 Molecular and Crystal-fragment Parameters

Tables S1 and S2 summarize the geometries, inertial parameters, and BF quadrupole components that we have assumed for the H_2 and H_2O moieties in computing the TR states of $H_2@C_{60}$ and $H_2O@C_{60}$, respectively.

Table S3 gives the C nuclear coordinates for the C_{60} "master-cage" geometry assumed for all the C_{60} moieties relevant to this work. The geometry has shared-hexagon (6:6) CC bond lengths equal to 2.60820 bohrs (1.38020 Å) and hexagon-pentagon (6:5) CC bond lengths equal to 2.73047 bohrs (1.44490 Å). The cage-fixed cartesian axis system is centered at the

C_{60} center of mass, has its z axis along one of the C_5 symmetry axes of the cage, and its x axis along one of the C_2 symmetry axes of the cage.

Tables S4 and S5 give the cage-center translation vectors ($\mathbf{T}(k)$) and the direction-cosine matrices ($\hat{R}(k)$) that define the positions and orientations of the thirteen cages in the P and H crystal fragments, respectively, w.r.t. the "space-fixed" (SF) cartesian axis system. These parameters conform to the C_{60} crystal geometries described in Sachidanandam and Harris[1] and Harris and Sachidanandam[2] for the angle ϕ (defined in those papers) equal to 24° (P orientation) and 84° (H orientation). The SF frame has its origin at the center of the central cage (cage #13) and is oriented such that the C_3 symmetry axis of the fragment is along the $(1, 1, 1)$ direction. To obtain the position vector, $\mathbf{R}_i$, of the *ith* C nucleus of cage k relative to the SF frame one uses

$$\mathbf{R}_i = \mathbf{T}(k) + \hat{R}(k)\mathbf{D}_i, \tag{1}$$

where $\mathbf{D}_i$ is the position vector, as given in Table S3, of the *ith* C nucleus in the cage-fixed axis system. In Tables S4 and S5, cages 1 to 6 are the "axial" and cages 7 to 12 are the "equatorial" cages in the fragment.

2 Basis sets, Grid Parameters, and Lennard-Jones Potential-Energy Parameters

2.1 H_2@C_{60}

2.1.1 Basis Functions

The basis functions employed in the variational calculations of the TR states of H_2@C_{60} are of the form $|n, l, m_l\rangle|j, m_j\rangle$.

The $|n, l, m_l\rangle$ are 3D isotropic harmonic-oscillator eigenfunctions:[3]

$$|n, l, m_l\rangle = N_{nl} R^l e^{-\beta R^2/2} L_k^{(l+1/2)}(\beta R^2) Y_{lm_l}(\Theta, \Phi), \tag{2}$$

where $\beta = 2.9888989$ au, $n = 0, 1, 2, \ldots, n_{\max}$, $l = n, n-2, \ldots \geq 0$, $k \equiv (n-l)/2$, $m_l = -l, (-l+1), \ldots, (l-1), l$,

$$N_{nl} = 2\left[\frac{\beta^{(2l+3/2)}2^{k+l}k!}{\sqrt{\pi}[2(k+l)+1]!!}\right]^{1/2}, \tag{3}$$

the $L_k^{(l+1/2)}$ are associated Laguerre polynomials, and the Y_{lm_l} are spherical harmonics. We used $n_{\max} = 8$.

The $|j, m_j\rangle$ are spherical harmonics

$$|j, m_j\rangle = Y_{jm_j}(\theta, \phi), \tag{4}$$

where $j = 0, 1, 2, \ldots, j_{\max}$ and $m_j = -j, (-j+1), \ldots, (j-1), j$. We used $j_{\max} = 8$.

2.1.2 Grid Parameters

The 5D grid described in Section 2.5 of the main body of the paper consists of (i) $N_a = 12$ Gauss-associated-Laguerre quadrature points R_a, generated as per Felker and Bačić[4] for $\beta = 2.9888989$ au, (ii) $N_b = 10$ Gauss-Legendre quadrature points $(\cos\beta)_b$, (iii) $N_c = 18$ Fourier grid points α_c, (iv) $N_d = 10$ Gauss-Legendre quadrature points $(\cos\theta)_d$, and (v) $N_e = 18$ Fourier grid points ϕ_e.

2.1.3 Kinetic-Energy Operator, $\hat{T}$

For H_2@C_{60} in the rigid-monomer approximation

$$\hat{T} = -\frac{\nabla^2}{2M} + \frac{\hat{J}^2}{2I}, \tag{5}$$

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 I is the moment of inertia of the H_2. The inertial parameters that we have employed are given in Table S1.

2.1.4 Lennard-Jones Potential-Energy Parameters

The V_{LJ} PES function appearing in $\hat{H}$ for $H_2@C_{60}$ is taken from Xu, et al.[5] and is given by

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

where i runs over the three H_2 sites listed in Table S1, 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, $w_1 = 6.7$, $w_2 = w_3 = 1$, $\sigma = 5.574692$ bohrs (2.95 Å), and $\epsilon = 3.07$ cm^{-1}. Of course, the r_{ik} depend on the position of the H_2 moiety w.r.t. the SF axes, so V_{LJ} is a function of $\mathbf{R}$ and ω.

2.2 $H_2O@C_{60}$

2.2.1 Basis Functions

The basis functions employed in the variational calculations of the TR states of $H_2O@C_{60}$ are of the form $|n, l, m_l\rangle|j, m_j, k\rangle$. The $|n, l, m_l\rangle$ are the same as for $H_2@C_{60}$ except that $\beta = 24.38$ au. The $|j, m_j, k\rangle$ are normalized Wigner rotation matrix elements

$$|j, m_j, k\rangle = \sqrt{\frac{2j+1}{8\pi^2}}[D^{(j)}_{m_j,k}(\phi, \theta, \chi)]^*, \tag{7}$$

where $j = 0, 1, 2, \ldots, j_{\max}$, $m_j = -j, (-j+1), \ldots, (j-1), j$, and $k = -j, (-j+1), \ldots, (j-1), j$. We used $j_{\max} = 8$.

2.2.2 Grid Parameters

The 6D grid described in Section 2.5 of the main body of the paper consisted of (i) $N_a = 12$ Gauss-associated-Laguerre quadrature points R_a, generated as per Felker and Bačić[4] for $\beta = 24.38$ au, (ii) $N_b = 10$ Gauss-Legendre quadrature points $(\cos\beta)_b$, (iii) $N_c = 18$ Fourier grid points α_c, (iv) $N_d = 10$ Gauss-Legendre quadrature points $(\cos\theta)_d$, and (v) $N_e = 18$ Fourier grid points ϕ_e, and (vi) $N_f = 18$ Fourier grid points χ_f.

2.2.3 Kinetic-Energy Operator, $\hat{T}$

For $H_2O@C_{60}$ in the rigid-monomer approximation

$$\hat{T} = -\frac{\nabla^2}{2M} + \sum_{k=x,y,z} \frac{\hat{J}_k^2}{2I_k}, \tag{8}$$

where ∇^2 is the Laplacian associated with $\mathbf{R}$, $\hat{J}_k^2$ is the operator corresponding to the square of the rotational angular momentum of the H_2O about its kth principal axis, M is the mass of the H_2O, and I_k is the moment of inertia of H_2O about its kth principal axis. The inertial parameters that we have employed are given in Table S2.

2.2.4 Lennard-Jones Potential-Energy Parameters

The V_{LJ} PES function appearing in $\hat{H}$ for $H_2O@C_{60}$ is taken from Felker and Bačić[8] and is given by

$$V_{LJ} = \sum_{i=1}^{3} \sum_{k=1}^{60} 4\epsilon_i \left[\left(\frac{\sigma_i}{r_{ik}} \right)^{12} - \left(\frac{\sigma_i}{r_{ik}} \right)^{6} \right], \tag{9}$$

where i runs over the three H_2O sites listed in Table S2, 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, $\sigma_1 = 6.37216$ bohrs (3.372 Å), $\sigma_2 = \sigma_3 = 4.988877$ bohrs (2.640 Å), $\epsilon_1 = 36.34$ cm^{-1}, and $\epsilon_2 = \epsilon_3 = 8.95384$ cm^{-1}. The r_{ik} depend on the position of the H_2O moiety w.r.t. the SF axes, so V_{LJ} is a function of $\mathbf{R}$ and ω.

3 Transformation properties of the electric-field-gradiant tensor, $I_m^{(2)}$

For arbitrary charge density $\rho(\mathbf{r})$ the internal moments of rank 2 (the components of the electric-field-gradient tensor) are given by[6]

$$I_m^{(2)} \equiv \int \frac{\rho(\mathbf{r})}{r^3} C_m^{(2)}(\hat{r}) d\mathbf{r} = \sqrt{\frac{4\pi}{5}} \int \frac{\rho(\mathbf{r})}{r^3} Y_{2m}(\hat{r}) d\mathbf{r}. \tag{10}$$

We examine below how these moments transform subject to (a) inversion through the origin and (b) rotation about an axis going through the origin.

3.1 Transformation by inversion

Inversion (operation E^*) changes the charge density $\rho(\mathbf{r})$ to $\rho'(\mathbf{r})$ such that

$$\rho'(\mathbf{r}) = \rho(-\mathbf{r}). \tag{11}$$

The internal moments corresponding to this new charge density are given by

$$\begin{aligned} I_m^{(2)}(E^*) &= \sqrt{\frac{4\pi}{5}} \int \frac{\rho'(\mathbf{r})}{r^3} Y_{2m}(\hat{r}) d\mathbf{r} = \sqrt{\frac{4\pi}{5}} \int \frac{\rho(-\mathbf{r})}{r^3} Y_{2m}(\hat{r}) d\mathbf{r} \\ &= \sqrt{\frac{4\pi}{5}} \int \frac{\rho(\mathbf{r}')}{r'^3} Y_{2m}(-\hat{r}') d\mathbf{r}', \end{aligned} \tag{12}$$

where we have substituted $\mathbf{r}' = -\mathbf{r}$ to obtain the final equality. Since $Y_{2m}(-\hat{r}') = Y_{2m}(\hat{r}')$, one sees from Eqs. (10) and (12) that

$$I_m^{(2)}(E^*) = I_m^{(2)}. \tag{13}$$

Inversion leaves internal moments of rank 2 unchanged.

3.2 Transformation by rotation about an axis through the origin

We start by expressing $\rho(\mathbf{r})$ as an expansion over spherical harmonics

$$\rho(\mathbf{r}) = \sum_{l,m} a_{lm}(r) Y_{lm}(\hat{r}), \tag{14}$$

where

$$a_{lm}(r) = \int \rho(\mathbf{r}) Y^*_{lm}(\hat{r}) d\hat{r}. \tag{15}$$

Next we substitute this expansion for $\rho(\mathbf{r})$ into Eq. (10) to obtain

$$\begin{aligned} I_m^{(2)} &= \sqrt{\frac{4\pi}{5}} \sum_{l,m'} \int \frac{a_{lm'}(r)}{r^3} Y_{lm'}(\hat{r}) Y_{2m}(\hat{r}) d\mathbf{r} \\ &= \sqrt{\frac{4\pi}{5}} (-)^m \int \frac{a_{2,-m}(r)}{r^3} dr, \end{aligned} \tag{16}$$

where the last equality in Eq. (16) follows from the orthonormality of the spherical harmonics and the fact that

$$Y^*_{lm} = (-)^m Y_{l,-m}. \tag{17}$$

Now we rotate the charge density $\rho(\mathbf{r})$ through an angle γ about an axis $\hat{n}$ going through the origin. The density is transformed as follows

$$e^{-i\hat{J}_n \gamma} \rho(\mathbf{r}) = \sum_{l,m} a_{lm}(r) [e^{-i\hat{J}_n \gamma} Y_{lm}(\hat{r})], \tag{18}$$

where $\hat{J}_n$ is the operator corresponding to angular momentum about $\hat{n}$.

Consider the new $I_m^{(2)}$ – call them $I_m^{(2)}(\hat{n}, \gamma)$ – corresponding to this rotated density

$$\begin{aligned} \sqrt{\frac{5}{4\pi}} I_m^{(2)}(\hat{n}, \gamma) &= \int \frac{[e^{-i\hat{J}_n \gamma} \rho(\mathbf{r})]}{r^3} Y_{2m}(\hat{r}) d\mathbf{r} \\ &= \sum_{l,m'} \int \frac{a_{l,m'}(r)}{r^3} dr \int [e^{-i\hat{J}_n \gamma} Y_{lm'}] Y_{2m} d\hat{r}. \end{aligned} \tag{19}$$

Now

$$e^{-i\hat{J}_n\gamma}Y_{lm'}(\hat{r}) = \sum_{m''} A^{(l)}_{m'',m'}(\hat{n},\gamma)Y_{lm''}(\hat{r}), \tag{20}$$

where

$$A^{(l)}_{m'',m'}(\hat{n},\gamma) \equiv \int Y^*_{lm''}(\hat{r})e^{-i\hat{J}_n\gamma}Y_{lm'}(\hat{r})d\hat{r}. \tag{21}$$

Substituting Eq. (20) into Eq. (19) one obtains

$$\begin{aligned} \sqrt{\frac{5}{4\pi}}I^{(2)}_m(\hat{n},\gamma) &= \sum_{l,m'}\left[\int \frac{a_{l,m'}(r)}{r^3}dr \times \sum_{m''} A^{(l)}_{m''m'}(\hat{n},\gamma)\int Y_{lm''}(\hat{r})Y_{2m}(\hat{r})d\hat{r}\right] \\ &= \sum_{m'}(-)^m A^{(2)}_{-m,m'}(\hat{n},\gamma)\int \frac{a_{2,m'}(r)}{r^3}dr. \end{aligned} \tag{22}$$

By using Eq. (16) one then obtains

$$I^{(2)}_m(\hat{n},\gamma) = \sum_{m'}(-)^{m+m'}A^{(2)}_{-m,m'}(\hat{n},\gamma)I^{(2)}_{-m'} = \sum_{m'}(-)^{m+m'}A^{(2)}_{-m,-m'}(\hat{n},\gamma)I^{(2)}_{m'}. \tag{23}$$

What remains is to evaluate the $A^{(2)}_{m,m'}(\hat{n},\gamma)$. If one specifies the direction of the axis $\hat{n}$ by its polar angle β and azimuthal angle α, it is straightforward to show that

$$A^{(l)}_{m,m'}(\alpha,\beta,\gamma) \equiv A^{(l)}_{m,m'}(\hat{n},\gamma) = e^{i(m'-m)\alpha}\sum_{m''} e^{-im''\gamma}d^{(l)}_{m,m''}(\beta)d^{(l)}_{m',m''}(\beta), \tag{24}$$

where the $d^{(l)}_{m,m'}(\beta)$ are little-d Wigner rotation matrix elements. From Eq. (24), one can also easily show that

$$(-)^{m+m'}A^{(l)}_{-m,-m'}(\hat{n},\gamma) = [A^{(l)}_{m,m'}(\hat{n},\gamma)]^* \tag{25}$$

and that

$$(-)^{m+m'}A^{(l)}_{-m,-m'}(\hat{n},-\gamma) = A^{(l)}_{m',m}(\hat{n},\gamma). \tag{26}$$

Finally, with Eqs. (23), (25), and (26)

$$I_m^{(2)}(\hat{n},\gamma) = \sum_{m'} [A_{m,m'}^{(2)}(\hat{n},\gamma)]^* I_{m'}^{(2)} \tag{27}$$

and

$$I_m^{(2)}(\hat{n},-\gamma) = \sum_{m'} A_{m',m}^{(2)}(\hat{n},\gamma) I_{m'}^{(2)}. \tag{28}$$

Relevant to the M@C_{60} crystal-fragment geometries in this work are the rotations by $\pm 2\pi/3$ about $\hat{n}$ when $\hat{n}$ lies along the $(1,1,1)$ direction, so that $\beta = \cos^{-1}(\sqrt{1/3})$ and $\alpha = \pi/4$. Evaluation of Eq. (24) for $\gamma = +2\pi/3$ about this axis and for $l = 2$ yields the matrix of values

$$\mathbf{B} \equiv \mathbf{A}^{(2)}(\pi/4, \cos^{-1}(\sqrt{1/3}), 2\pi/3) = \begin{pmatrix} -\frac{1}{4} & \frac{1}{2} & -\sqrt{\frac{3}{8}} & \frac{1}{2} & -\frac{1}{4} \\ \frac{i}{2} & -\frac{i}{2} & 0 & \frac{i}{2} & -\frac{i}{2} \\ \sqrt{\frac{3}{8}} & 0 & -\frac{1}{2} & 0 & \sqrt{\frac{3}{8}} \\ -\frac{i}{2} & -\frac{i}{2} & 0 & \frac{i}{2} & \frac{i}{2} \\ -\frac{1}{4} & -\frac{1}{2} & -\sqrt{\frac{3}{8}} & -\frac{1}{2} & -\frac{1}{4} \end{pmatrix}, \tag{29}$$

where the rows run from $m = -2$ to 2 and the columns from $m' = -2$ to 2.

3.3 Invariant $I_m^{(2)}$ for the M@C_{60} Crystal Fragment

For this work we take the P and H crystal fragments to be invariant under the operations of the S_6 point group. In addition, we have chosen SF cartesian axes such that the C_3 symmetry axis of S_6 points along the $(1,1,1)$ direction. Since the internal moments due to the NN cages must be invariant to a $2\pi/3$ rotation about the C_3 axis, then given Eqs. (27)

and (29), the following must be obeyed

$$\mathbf{B}^* I^{(2)} = I^{(2)}, \tag{30}$$

where $I^{(2)}$ is the column vector composed of internal moments produced by the charge density of the twelve NN cages

$$I^{(2)} \equiv \begin{pmatrix} I^{(2)}_{-2} \\ \\ I^{(2)}_{-1} \\ \\ I^{(2)}_{0} \\ \\ I^{(2)}_{+1} \\ \\ I^{(2)}_{+2} \end{pmatrix} . \tag{31}$$

Equation (30) is satisfied if $I^{(2)}$ is an eigenvector of $\mathbf{B}^*$ having eigenvalue equal to $+1$. These eigenvectors can be straightforwardly determined. They are given by

$$I^{(2)} = A \begin{pmatrix} i \\ \\ (-1+i) \\ \\ 0 \\ \\ (1+i) \\ \\ -i \end{pmatrix} , \tag{32}$$

where, in general, A is a complex constant.

4 Perturbation theory applied to $j = 1$ level splittings

4.1 H_2@C_{60} and HF@C_{60}

We take the lowest-energy zeroth-order TR states of H_2@C_{60} and HF@C_{60} to be of the form $|T_0\rangle|j, m_j\rangle$,[7] where $|T_0\rangle$ depends only on $\mathbf{R}$ and $|j, m_j\rangle$ is a rigid-rotor rotational eigenfunction. The matrix elements of V_{quad} connecting the states of a given j level are then given by

$$\langle T_0, j, m_j'|V_{\text{quad}}|T_0, j, m_j\rangle = \sum_m (-)^m I_{-m}^{(2)} \langle T_0, j, m_j'|Q_m^{(2)}|T_0, j, m_j\rangle. \tag{33}$$

By using Eq. (15) of the main text

$$\begin{aligned} \langle T_0, j, m_j'|Q_m^{(2)}|T_0, j, m_j\rangle &= Q_0^{\text{BF}} \langle j, m_j'|[D_{m,0}^{(2)}(\omega)]^*|j, m_j\rangle \\ &+ (-)^m \sqrt{40\pi}\mu_z \sum_{m'} \begin{pmatrix} 1 & 1 & 2 \\ m' & m-m' & -m \end{pmatrix} \\ &\times \langle T_0|RY_{1,m'}(\Theta,\Phi)|T_0\rangle \langle j, m_j'|[D_{m-m',0}^{(1)}(\omega)]^*|j, m_j\rangle. \end{aligned} \tag{34}$$

Now the $|T_0, j, m_j\rangle$ have inversion symmetry (due to the I_h environment imposed by the central C_{60} cage), as do the $|j, m_j\rangle$. In consequence, $|T_0\rangle$ also has inversion symmetry. The upshot is that the factors $\langle T_0|RY_{1,m'}(\Theta,\Phi)|T_0\rangle$ appearing in Eq. (34) are zero by symmetry, since $RY_{1m'}(\Theta,\Phi)$ changes sign upon inversion. Thus we need only consider the first term on the rhs of Eq. (34). One finds

$$\langle T_0, j, m_j'|Q_m^{(2)}|T_0, j, m_j\rangle = (-)^{m_j'}(2j+1)Q_0^{\text{BF}} \begin{pmatrix} j & j & 2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j & j & 2 \\ -m_j' & m_j & m \end{pmatrix}. \tag{35}$$

Substituting Eq. (35) into Eq. (33) one obtains

$$\begin{aligned}\langle T_0, j, m_j'|V_{\text{quad}}|T_0, j, m_j\rangle &= (-)^{m_j} I^{(2)}_{m_j - m_j'} \begin{pmatrix} j & j & 2 \\ -m_j' & m_j & m_j' - m_j \end{pmatrix} \\ & \times (2j+1) Q_0^{\text{BF}} \begin{pmatrix} j & j & 2 \\ 0 & 0 & 0 \end{pmatrix}. \end{aligned} \tag{36}$$

These matrix elements are readily evaluated for a given value of j. For $j = 1$ the full matrix (rows labeled by $m_j' = -1, 0, 1$ and columns by $m_j = -1, 0, 1$) is given by

$$\langle T_0, 1, \{m_j'\}|V_{\text{quad}}|T_0, 1, \{m_j\}\rangle = \frac{\sqrt{6}}{5} Q_0^{\text{BF}} A \begin{pmatrix} 0 & -\frac{(1+i)}{\sqrt{2}} & i \\ -\frac{(1-i)}{\sqrt{2}} & 0 & \frac{(1+i)}{\sqrt{2}} \\ -i & \frac{(1-i)}{\sqrt{2}} & 0 \end{pmatrix}, \tag{37}$$

where we have used Eq. (32) for the $I_m^{(2)}$. This matrix has eigenvalues $\frac{\sqrt{6}}{5} Q_0^{\text{BF}} A$, $\frac{\sqrt{6}}{5} Q_0^{\text{BF}} A$, and $-2\frac{\sqrt{6}}{5} Q_0^{\text{BF}} A$. These are the first-order corrections to the energies of the $j = 1$ states and give

$$\Delta_{\text{PT}} \equiv E(g = 2) - E(g = 1) = 3A\frac{\sqrt{6}}{5} Q_0^{\text{BF}}, \tag{38}$$

consistent with Eqs. (17) and (18) of the main text.

4.2 $H_2O@C_{60}$

For $H_2O@C_{60}$ the lowest-energy zeroth-order states[8] are very well-approximated by $|T_0\rangle|j_{k_a k_c}, m_j\rangle$, where $|T_0\rangle$ depends only on $\mathbf{R}$,

$$|j_{k_a k_c}, m_j\rangle = \sum_k a(j_{k_a k_c}, k)|j, m_j, k\rangle \tag{39}$$

is an eigenfunction of the rigid-H_2O rotational Hamiltonian, and the $|j, m_j, k\rangle$ are symmetric-top rotational eigenfunctions

$$|j, m_j, k\rangle = \sqrt{\frac{2j+1}{8\pi^2}}[D^{(j)}_{m_j,k}(\omega)]^*. \tag{40}$$

Matrix elements of $V_{\rm quad}$ connecting states of a given $|T_0, j_{k_a k_c}\rangle$ level are given by

$$\langle T_0, j_{k_a k_c}, m'_j|V_{\rm quad}|T_0, j_{k_a k_c}, m_j\rangle = \sum_m (-)^m I^{(2)}_{-m}\langle T_0, j_{k_a k_c}, m'_j|Q^{(2)}_m|T_0, j_{k_a k_c}, m_j\rangle. \tag{41}$$

To evaluate the matrix elements on the rhs of Eq. (41) we use Eq. (15) of the main text and note that, as for H_2 and HF, $|T_0\rangle$ has definite parity. Thus,

$$\langle T_0|RY_{1,m'}(\Theta, \Phi)|T_0\rangle = 0 \tag{42}$$

and

$$\langle T_0, j_{k_a k_c}, m'_j|Q^{(2)}_m|T_0, j_{k_a k_c}, m_j\rangle = \sum_{q=-2}^{2} Q^{\rm BF}_q \langle j_{k_a k_c}, m'_j|[D^{(2)}_{m,q}]^*|j_{k_a k_c}, m_j\rangle. \tag{43}$$

By using Eqs. (39) and (40)

$$\begin{aligned}
\langle j_{k_a k_c}, m'_j|[D^{(2)}_{m,q}]^*|j_{k_a k_c}, m_j\rangle &= \sum_{k,k'} a(j_{k_a k_c}, k')a(j_{k_a k_c}, k)\langle j, m'_j, k'|[D^{(2)}_{m,q}]^*|j, m_j, k\rangle \\
&= (-)^{m'_j}(2j+1)\begin{pmatrix} j & j & 2 \\ -m'_j & m_j & m \end{pmatrix} \\
&\times \sum_{k,k'}(-)^{k'} a(j_{k_a k_c}, k')a(j_{k_a k_c}, k)\begin{pmatrix} j & j & 2 \\ -k' & k & q \end{pmatrix}.
\end{aligned} \tag{44}$$

Substituting Eq. (44) into Eq. (43) and then the latter into Eq. (41) one obtains

$$\langle T_0, j_{k_a k_c}, m_j' | V_{\rm quad} | T_0, j_{k_a k_c}, m_j \rangle = (-)^{m_j} I^{(2)}_{m_j - m_j'} \begin{pmatrix} j & j & 2 \\ -m_j' & m_j & m_j' - m_j \end{pmatrix}$$
$$\times (2j+1) \sum_q Q_q^{\rm BF} \sum_{k',k} (-)^{k'} a(j_{k_a k_c}, k') a(j_{k_a k_c}, k) \begin{pmatrix} j & j & 2 \\ -k' & k & q \end{pmatrix}. \tag{45}$$

For $j = 1$ the Eq.-(45) matrix (rows labeled by $m_j' = -1, 0, 1$ and columns by $m_j = -1, 0, 1$) is given by

$$\langle T_0, 1_{k_a k_c}, \{m_j'\} | V_{\rm quad} | T_0, 1_{k_a k_c}, \{m_j\} \rangle = A f(Q^{\rm BF}) \begin{pmatrix} 0 & -\frac{(1+i)}{\sqrt{2}} & i \\ -\frac{(1-i)}{\sqrt{2}} & 0 & \frac{(1+i)}{\sqrt{2}} \\ -i & \frac{(1-i)}{\sqrt{2}} & 0 \end{pmatrix}, \tag{46}$$

where we have used Eq. (32) for the $I_m^{(2)}$ and

$$f(Q^{\rm BF}) \equiv \frac{3}{\sqrt{5}} \left[\sum_q Q_q^{\rm BF} \sum_{k',k} (-)^{k'} a(j_{k_a k_c}, k') a(j_{k_a k_c}, k) \begin{pmatrix} 1 & 1 & 2 \\ -k' & k & q \end{pmatrix} \right]. \tag{47}$$

Diagonalization of Eq. (46) yields the eigenvalues $Af(Q^{\rm BF})$, $Af(Q^{\rm BF})$, and $-2Af(Q^{\rm BF})$ and the level splitting

$$\Delta_{\rm PT} = E(g=2) - E(g=1) = 3Af(Q^{\rm BF}). \tag{48}$$

For the 1_{01} level, the *ortho* ground state,

$$a(1_{01}, 1) = -a(1_{01}, -1) = \frac{1}{\sqrt{2}} \qquad a(1_{01}, 0) = 0 \tag{49}$$

and

$$f(Q^{\mathrm{BF}}, 1_{01}) = \frac{3}{5}\Big[-\frac{1}{\sqrt{6}}Q_0^{\mathrm{BF}} + \frac{1}{2}\big(Q_2^{\mathrm{BF}} + Q_{-2}^{\mathrm{BF}}\big)\Big]. \tag{50}$$

For the first excited rotational state of the *ortho* species, 1_{10},

$$a(1_{01}, 1) = a(1_{01}, -1) = \frac{1}{\sqrt{2}} \qquad a(1_{01}, 0) = 0 \tag{51}$$

and

$$f(Q^{\mathrm{BF}}, 1_{10}) = \frac{3}{5}\Big[+\frac{1}{\sqrt{6}}Q_0^{\mathrm{BF}} + \frac{1}{2}\big(Q_2^{\mathrm{BF}} + Q_{-2}^{\mathrm{BF}}\big)\Big]. \tag{52}$$

Finally, for the first excited rotational state of the *para* species, 1_{11},

$$a(1_{11}, 1) = a(1_{11}, -1) = 0 \qquad a(1_{11}, 0) = 1 \tag{53}$$

and

$$f(Q^{\mathrm{BF}}, 1_{11}) = \frac{\sqrt{6}}{5}Q_0^{\mathrm{BF}}. \tag{54}$$

References

(1) R. Sachidanandam and A. B. Harris, Phys. Rev. Lett. **67**, 1467 (1991).

(2) A. B. Harris and R. Sachidanandam, Phys. Rev. B **46**, 4944 (1992).

(3) For example, see https://en.wikipedia.org/wiki/Quantum_harmonic_oscillator

(4) See P. M. Felker and Z. Bačić, J. Chem. Phys. **145**, 084310 (2016), Supplementary Material, Section II.

(5) M. Xu, S. Ye, A. Powers, R. Lawler, N. J. Turro, and Z. Bačić , J. Chem. Phys. **139**, 064309 (2013).

(6) For example, For example, R. N. Zare, *Angular Momentum* (Wiley, New York, 1988), Eq. (7), p. 246.

(7) For example, M. Xu, F. Sebastianelli, Z. Bačić, R. Lawler, and N. J. Turro, J. Chem. Phys. **128**, 011101 (2008).

(8) P. M. Felker and Z. Bačić, J. Chem. Phys. **145**, 084310 (2016).

Table 1: H_2 BF site coordinates (in bohrs), site masses (in amu), rotational constant (in cm^{-1}), and BF quadrupole (in au).

Site #	x	y	z	mass
1	0.000000	0.000000	0.000000	0.0000
2	0.000000	0.000000	+0.699199	1.0078
3	0.000000	0.000000	−0.699199	1.0078

$$(2I)^{-1} = 58.378$$

$$Q_0^{\mathrm{BF}} = 0.499$$

Table 2: H_2O BF site coordinates (in bohrs), site masses (in amu), rotational constants (in cm^{-1}), and BF quadrupole and dipole components (in au).

Site #	x	y	z	mass
1	0.000000	0.000000	0.125534	15.9949
2	1.453650	0.000000	-0.996156	1.0078
3	-1.453650	0.000000	-0.996156	1.0078
$(2I_x)^{-1}$	$(2I_y)^{-1}$	$(2I_z)^{-1}$		
27.877	9.285	14.512		
$Q_0^{(\mathrm{BF})}$	$Q_{\pm 2}^{(\mathrm{BF})}$	$\vec{\mu} = \mu \hat{z}$		
-0.09973	1.53843	-0.737196		

Table 3: Carbon nuclear coordinates (in bohrs) for the "master cage" C_{60} geometry. Coordinates are referenced to a cage-fixed cartesian axis system having its origin at the center of the cage, its z axis along one of the C_5 symmetry axes of the cage, and its x axis along one of the C_2 symmetry axes of the cage.

C nucleus	x	y	z
1	0.000000	2.322672	6.238707
2	−2.208993	0.717744	6.238707
3	−1.365233	−1.879081	6.238707
4	1.365233	−1.879081	6.238707
5	2.208993	0.717744	6.238707
6	4.319071	1.403350	4.867496
7	5.684303	−0.475731	3.432005
8	4.878326	−2.956276	3.432005
9	2.669332	−3.674020	4.867496
10	1.304100	−5.553102	3.432005
11	−1.304100	−5.553102	3.432005
12	−2.669332	−3.674020	4.867496
13	−4.878326	−2.956276	3.432005
14	−5.684303	−0.475731	3.432005
15	−4.319071	1.403350	4.867496
16	−4.319071	3.726024	3.432005
17	−5.684303	3.282433	1.109333
18	−6.528064	0.685606	1.109333
19	−6.528064	−0.685606	−1.109333
20	−5.684303	−3.282433	−1.109333
21	−4.878326	−4.391767	1.109333
22	−2.669332	−5.996694	1.109333
23	−1.365233	−6.420422	−1.109333

24	1.365233	−6.420422	−1.109333
25	2.669332	−5.996694	1.109333
26	4.878326	−4.391767	1.109333
27	5.684303	−3.282433	−1.109333
28	6.528064	−0.685606	−1.109333
29	6.528064	0.685606	1.109333
30	5.684303	3.282433	1.109333
31	4.878326	4.391767	−1.109333
32	4.878326	2.956276	−3.432005
33	5.684303	0.475731	−3.432005
34	4.319071	−1.403350	−4.867496
35	4.319071	−3.726024	−3.432005
36	2.208993	−5.259085	−3.432005
37	0.000000	−4.541340	−4.867496
38	−2.208993	−5.259085	−3.432005
39	−4.319071	−3.726024	−3.432005
40	−4.319071	−1.403350	−4.867496
41	−5.684303	0.475731	−3.432005
42	−4.878326	2.956276	−3.432005
43	−4.878326	4.391767	−1.109333
44	−2.669332	5.996694	−1.109333
45	−1.304100	5.553102	−3.432005
46	−2.669332	3.674020	−4.867496
47	−1.365233	1.879081	−6.238707
48	−2.208993	−0.717744	−6.238707
49	0.000000	−2.322672	−6.238707
50	2.208993	−0.717744	−6.238707

51	1.365233	1.879081	−6.238707
52	2.669332	3.674020	−4.867496
53	1.304100	5.553102	−3.432005
54	2.669332	5.996694	−1.109333
55	1.365233	6.420422	1.109333
56	−1.365233	6.420422	1.109333
57	−2.208993	5.259085	3.432005
58	0.000000	4.541340	4.867496
59	2.208993	5.259085	3.432005
60	4.319071	3.726024	3.432005

Table 4: Cage center translation vector, $\mathbf{T}$ (in bohrs) and rotation matrix, $\hat{R}$, defining the position of each of the cages in the 13-cage fragment corresponding to the P orientation of M@$C_{60}(s)$.

Cage # (k)	$\mathbf{T}(k)$	$\hat{R}(k)$
1	$(13.265878, 0.000000, 13.265878)$	$\begin{pmatrix} 0.556377 & -0.457993 & -0.693316 \\ -0.566903 & 0.400811 & -0.719702 \\ 0.607508 & 0.793469 & -0.036636 \end{pmatrix}$
2	$(0.000000, 13.265878, 13.265878)$	$\begin{pmatrix} 0.556377 & -0.457993 & -0.693316 \\ 0.566903 & -0.400811 & 0.719702 \\ -0.607508 & -0.793469 & 0.036636 \end{pmatrix}$
3	$(13.265878, 13.265878, 0.000000)$	$\begin{pmatrix} -0.556377 & 0.457993 & 0.693316 \\ -0.566903 & 0.400811 & -0.719702 \\ -0.607508 & -0.793469 & 0.036636 \end{pmatrix}$
4	$(-13.265878, 0.000000, -13.265878)$	$\begin{pmatrix} 0.556377 & -0.457993 & -0.693316 \\ -0.566903 & 0.400811 & -0.719702 \\ 0.607508 & 0.793469 & -0.036636 \end{pmatrix}$
5	$(0.000000, -13.265878, -13.265878)$	$\begin{pmatrix} 0.556377 & -0.457993 & -0.693316 \\ 0.566903 & -0.400811 & 0.719702 \\ -0.607508 & -0.793469 & 0.036636 \end{pmatrix}$

6	$(-13.265878, -13.265878, 0.000000)$	$\begin{pmatrix} -0.556377 & 0.457993 & 0.693316 \\ -0.566903 & 0.400811 & -0.719702 \\ -0.607508 & -0.793469 & 0.036636 \end{pmatrix}$
7	$(0.000000, 13.265878, -13.265878)$	$\begin{pmatrix} 0.556377 & -0.457993 & -0.693316 \\ 0.566903 & -0.400811 & 0.719702 \\ -0.607508 & -0.793469 & 0.036636 \end{pmatrix}$
8	$(13.265878, 0.000000, -13.265878)$	$\begin{pmatrix} 0.556377 & -0.457993 & -0.693316 \\ -0.566903 & 0.400811 & -0.719702 \\ 0.607508 & 0.793469 & -0.036636 \end{pmatrix}$
9	$(0.000000, -13.265878, 13.265878)$	$\begin{pmatrix} 0.556377 & -0.457993 & -0.693316 \\ 0.566903 & -0.400811 & 0.719702 \\ -0.607508 & -0.793469 & 0.036636 \end{pmatrix}$
10	$(13.265878, -13.265878, 0.000000)$	$\begin{pmatrix} -0.556377 & 0.457993 & 0.693316 \\ -0.566903 & 0.400811 & -0.719702 \\ -0.607508 & -0.793469 & 0.036636 \end{pmatrix}$
11	$(-13.265878, 0.000000, 13.265878)$	$\begin{pmatrix} 0.556377 & -0.457993 & -0.693316 \\ -0.566903 & 0.400811 & -0.719702 \\ 0.607508 & 0.793469 & -0.036636 \end{pmatrix}$
12	$(-13.265878, 13.265878, 0.000000)$	$\begin{pmatrix} -0.556377 & 0.457993 & 0.693316 \\ -0.566903 & 0.400811 & -0.719702 \\ -0.607508 & -0.793469 & 0.036636 \end{pmatrix}$

13	$(0.000000, 0.000000, 0.000000)$	$\begin{pmatrix} -0.556377 & 0.457993 & 0.693316 \\ 0.566903 & -0.400811 & 0.719702 \\ 0.607508 & 0.793469 & -0.036636 \end{pmatrix}$

Table 5: Cage center translation vector, $\mathbf{T}$ (in bohrs) and rotation matrix, $\hat{R}$, defining the position of each of the cages in the 13-cage fragment corresponding to the H orientation of M@$C_{60}(s)$.

Cage # (k)	$\mathbf{T}(k)$	$\hat{R}(k)$
1	$(13.265878, 0.000000, 13.265878)$	$\begin{pmatrix} 0.154881 & -0.967912 & -0.197886 \\ 0.195485 & 0.226368 & -0.954224 \\ 0.968400 & 0.109107 & 0.224272 \end{pmatrix}$
2	$(0.000000, 13.265878, 13.265878)$	$\begin{pmatrix} 0.154881 & -0.967912 & -0.197886 \\ -0.195485 & -0.226368 & 0.954224 \\ -0.968400 & -0.109107 & -0.224272 \end{pmatrix}$
3	$(13.265878, 13.265878, 0.000000)$	$\begin{pmatrix} -0.154881 & 0.967912 & 0.197886 \\ 0.195485 & 0.226368 & -0.954224 \\ -0.968400 & -0.109107 & -0.224272 \end{pmatrix}$
4	$(-13.265878, 0.000000, -13.265878)$	$\begin{pmatrix} 0.154881 & -0.967912 & -0.197886 \\ 0.195485 & 0.226368 & -0.954224 \\ 0.968400 & 0.109107 & 0.224272 \end{pmatrix}$
5	$(0.000000, -13.265878, -13.265878)$	$\begin{pmatrix} 0.154881 & -0.967912 & -0.197886 \\ -0.195485 & -0.226368 & 0.954224 \\ -0.968400 & -0.109107 & -0.224272 \end{pmatrix}$

6	$(-13.265878, -13.265878, 0.000000)$	$\begin{pmatrix} -0.154881 & 0.967912 & 0.197886 \\ 0.195485 & 0.226368 & -0.954224 \\ -0.968400 & -0.109107 & -0.224272 \end{pmatrix}$
7	$(0.000000, 13.265878, -13.265878)$	$\begin{pmatrix} 0.154881 & -0.967912 & -0.197886 \\ -0.195485 & -0.226368 & 0.954224 \\ -0.968400 & -0.109107 & -0.224272 \end{pmatrix}$
8	$(13.265878, 0.000000, -13.265878)$	$\begin{pmatrix} 0.154881 & -0.967912 & -0.197886 \\ 0.195485 & 0.226368 & -0.954224 \\ 0.968400 & 0.109107 & 0.224272 \end{pmatrix}$
9	$(0.000000, -13.265878, 13.265878)$	$\begin{pmatrix} 0.154881 & -0.967912 & -0.197886 \\ -0.195485 & -0.226368 & 0.954224 \\ -0.968400 & -0.109107 & -0.224272 \end{pmatrix}$
10	$(13.265878, -13.265878, 0.000000)$	$\begin{pmatrix} -0.154881 & 0.967912 & 0.197886 \\ 0.195485 & 0.226368 & -0.954224 \\ -0.968400 & -0.109107 & -0.224272 \end{pmatrix}$
11	$(-13.265878, 0.000000, 13.265878)$	$\begin{pmatrix} 0.154881 & -0.967912 & -0.197886 \\ 0.195485 & 0.226368 & -0.954224 \\ 0.968400 & 0.109107 & 0.224272 \end{pmatrix}$
12	$(-13.265878, 13.265878, 0.000000)$	$\begin{pmatrix} -0.154881 & 0.967912 & 0.197886 \\ 0.195485 & 0.226368 & -0.954224 \\ -0.968400 & -0.109107 & -0.224272 \end{pmatrix}$

13	$(0.000000, 0.000000, 0.000000)$	$\begin{pmatrix} -0.154881 & 0.967912 & 0.197886 \\ -0.195485 & -0.226368 & 0.954224 \\ 0.968400 & 0.109107 & 0.224272 \end{pmatrix}$