Inelastic neutron scattering spectra of a hydrogen molecule in a nanocavity: Methodology for quantum calculations incorporating the coupled five-dimensional translation-rotation eigenstates

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Inelastic neutron scattering spectra of a hydrogen molecule in a nanocavity: Methodology for quantum calculations incorporating the coupled five-dimensional translation-rotation eigenstates

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We present an in-depth description of the methodology for accurate quantum calculation of the inelastic neutron scattering (INS) spectra of an H_2 molecule confined inside a nanosize cavity of an arbitrary shape. This methodology was introduced in a recent work [Xu, Ulivi, Celli, Colognesi, and Bačić, Phys. Rev. B **83**, 241403(R) (2011)], where the INS spectra of *para*- and *ortho*-H_2 in the small cage of the structure II clathrate hydrate were simulated and compared with the measured spectra. The key distinctive feature of our approach, and its main strength and advantage, is the use of the coupled quantum 5D translation-rotation (TR) energy levels and wave functions of the entrapped H_2 molecule, rigorously calculated on the 5D intermolecular potential energy surface (PES), as the initial and the final states of the INS transitions. In this work, we describe the implementation of the 5D TR wave functions within the quantum INS formalism, and obtain the working expressions for the matrix elements required to compute the INS spectra of the nanoconfined H_2 molecule. The computational approach devised for efficient calculation of the 5D TR eigenstates in the compact contracted basis, indispensable for our quantum simulation of the INS spectra, is presented as well. Since the TR coupling is fully taken into account, the computed INS spectra exhibit a uniquely high degree of realism and faithfully reflect the quantum dynamics of H_2 on the PES of the host environment.

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I. INTRODUCTION

Inelastic neutron scattering (INS) spectroscopy is a powerful tool for elucidating with atomistic resolution the behavior of molecular hydrogen inside the nanoscale cavities of a broad range of host materials. The unrivaled ability of the INS to reveal the details of the dynamics, spatial distribution and binding sites of hydrogen molecules within the nanocavity, and their interactions with the host, largely stems from two unique features. One of them is that the cross section for the incoherent neutron scattering from the hydrogen (^{1}H) nucleus is $\sim$15 times larger than for the nucleus of any other element, including the isotope deuterium (^{2}H). Consequently, if H atoms are present in the compound, the bands associated with their motions will dominate the spectrum.[1,2] This makes INS a highly selective probe of the dynamics of the confined guest H$_2$ (and HD) molecules; the H atoms of the host material, if any, can be selectively deuterated, thus suppressing their contribution to the spectra. The second distinctive feature of the INS is its ability to induce change in the total nuclear spin I of the hydrogen molecule, something which photons cannot do. As a result, rotational $\Delta J = 1$ transitions can be observed, such as $J = 0 \rightarrow 1$ of *para*-H$_2$ ($I = 0$) and $J = 1 \rightarrow 2$ of *ortho*-H$_2$ ($I = 1$). In contrast, $\Delta J = $ odd transition are forbidden in optical, infrared (IR) and Raman, spectroscopy of H$_2$, since they involve the *ortho-para* conversion.

INS spectroscopy has been utilized to gain fundamental understanding of the properties of molecular hydrogen entrapped in chemically highly diverse materials,[1] ranging from fullerenes[3–5] and clathrate hydrates[6,7] to metal-organic frameworks (MOFs)[8–11] and zeolites.[12,13] However, typically only a fraction of the rich information content of the INS spectra could be extracted and decoded, largely due to the limitations of the low-dimensional theoretical methods employed in their analysis. This is vividly illustrated by the INS spectra of hydrogen molecules in MOFs, where the potential energy landscape on which they move is complex, characterized by multiple minima corresponding to different binding sites. The observed INS peaks have been only partially, and tentatively, assigned to the rotational excitations of H$_2$ at different binding sites by matching their energies to the eigenvalues of a single-parameter phenomenological model for the rotational potential.[8,9,13] Assignments of this kind were inevitably inconclusive and also incomplete, since the excitations of H$_2$ center-of-mass (c.m.) translation were not considered at all.

Recently, for H$_2$ in two different MOFs, HKUST-1[10] and MOF-74,[14] two-dimensional (2D) angular (orientational) potential energy surfaces (PESs) were determined *ab initio*, with the H$_2$ c.m. fixed at one or two binding sites, for which the low-lying rotational energy levels were calculated. In addition, 1D translational potential curves were obtained *ab initio* along certain directions, for fixed H$_2$ orientations; their energy levels were calculated, giving approximate translational fundamental excitations. The transitions calculated in this way proved helpful for assigning some of the peaks in the INS spectra. However, the limitations of this reduced-dimension approach became apparent as well. For H$_2$ in both MOFs, the calculated translational and rotational energy levels were found to be close in energy,[10,14] "making the interpretation of the INS data difficult."[10] Indeed, this strongly suggested that treating the rotational and translational degrees of freedom of H$_2$ as separable, uncoupled, is not justified on physical grounds, and is likely to introduce errors of unknown magnitude in the computed excitation energies (the same can be said for taking the three translational degrees of freedom to be separable as well[10,14]). Moreover, in the case of H$_2$@HKUST-1, the computed 1D translational potential energy curves showed pronounced dependence on the H$_2$ orientation, providing additional evidence for large translation-rotation (TR) coupling, which cannot be ignored.[10]

That the three translational and the two rotational degrees of freedom of a nanoconfined H$_2$ molecule are in fact all intricately coupled, with clear manifestations in the TR energy level structure, was demonstrated by us several years earlier. In a series of papers we have conducted quantitative investigations of the quantum TR dynamics of the nanoconfined H$_2$ molecule(s), in which the TR coupling was treated rigorously. The systems considered include one or more hydrogen molecules encapsulated in the small[15,16] and large cages[17,18] of the structure II (sII) clathrate hydrate, and subsequently, inside the fullerenes C$_{60}$,[5,19–21] C$_{70}$,[20,21] and aza-thia-open-cage fullerene (ATOCF).[22] For H$_2$/HD in the small cage of sII clathrate hydrate[16] and H$_2$ in ATOCF,[22] we made direct comparison between the fully coupled TR excitation energies from the quantum 5D calculations and the measured INS spectra,[3,6] which shed additional light on the interpretation of the observed rotational and translational excitations. Owing to these recent developments, it is no longer necessary to resort to either phenomenological or decoupled reduced-dimension treatments whose accuracy is problematic. The quantum 5D TR energy levels and wave functions can now be calculated rigorously, as fully coupled, for H$_2$/HD/D$_2$ in any (rigid) nanocavity of arbitrary shape, provided that the 5D intermolecular PES is available.

The profound influence which the shape and symmetry of the nanocavity exert on the TR energy levels and their degeneracy patterns, and hence the INS spectra, of the caged H$_2$ molecule was demonstrated most vividly in our comparative study[20] of the quantum TR dynamics of H$_2$ in C$_{60}$ and C$_{70}$. The symmetry of C$_{70}$, D_{5h}, is much lower than that of C$_{60}$, I_h. As a result, the profile of the 5D PES of H$_2$ in C$_{70}$ in the direction of the long (z) molecular axis coinciding with the C_5 axis of rotation is very different from the potential cuts along the two equivalent short (x and y) axes perpendicular to it. The pronounced anisotropy of the PES with respect to the direction of the motion of the c.m. of H$_2$ inside C$_{70}$ stands in sharp contract to the PES of H$_2$ in C$_{60}$, whose directional, or radial, anisotropy

is very weak. The consequence of this is that the TR energy level structure of H_2 in C_{70} differs completely, both qualitatively and quantitatively, from that for H_2 in C_{60}, and requires an entirely different set of quantum numbers for its assignment.[20] For example, for H_2 in C_{60}, the translational fundamental (at 183.47 cm^{-1}) is triply degenerate, but for H_2 in C_{70} it is partially split into the z-mode fundamental (54.15 cm^{-1}) and the doubly degenerate 2D xy-mode fundamental (138.74 cm^{-1}).[20] These differences persist for higher translational excitations. Likewise, the $j = 1$ and $j = 2$ rotational levels of H_2 in C_{70} are partially split in $1 : 2$ and $1 : 2 : 2$ degeneracy patterns, respectively, already in the ground translational state, unlike in C_{60} where they fully retain their $(2j + 1)$-fold degeneracy. In addition, the level patterns (and energies) arising from the TR coupling when H_2 in C_{70} is translationally excited are totally unlike those for $H_2@C_{60}$.[20] It should be evident from the above that the INS spectra of H_2 in C_{60} and C_{70} will differ greatly in both the number of observed transitions and their energies.

The TR transitions present in the INS spectra, in addition to their energies, are characterized by their (relative) intensities. Together, the energies of the transitions and their intensity patterns constitute a unique fingerprint, reflecting the underlying quantum TR dynamics of the caged guest molecule and its interactions with the host. Clearly, the interpretation and assignment of the measured INS spectra would be much more reliable and complete if the theory can provide with confidence not only the TR excitation energies but their intensities as well, for comparison with the experimental data. Surprisingly little was done in this direction prior to our work described below. The few calculations of the INS spectra of H_2 in zeolites[23,24] treated the translational motion of H_2 as classical, which is inadequate at the low temperatures of interest, and the H_2 rotations quantum mechanically. An additional shortcoming of such a mixed quantum-classical approach is that it cannot describe the quantized translational excitations. The quantum treatments in the literature of the INS from molecular systems, primarily intended for the weakly interacting molecular hydrogen in the solid,[25,26] liquid,[27,28] and gas phase,[27] all make the approximation that the translational and rotational motions of the molecule are decoupled; as discussed above, this assumption is not justified for H_2 inside a nanocage.

Recently, we introduced[29] the quantum methodology for accurate calculation of the INS spectra, i.e., the energies and the intensities of the TR transitions, of an H_2 molecule confined in a nanocavity, in which the TR coupling is rigorously included. While our treatment rests on the standard basic equations of INS theory,[25,30] what makes it unique is that, unlike all previous treatments, it incorporates the fully coupled quantum 5D TR energy levels and wave functions of the entrapped H_2 molecule as the initial and final states of the INS transitions. As a result, the simulated INS spectra have the degree of realism that was not achieved before, and reflect faithfully the complexity of the quantum TR dynamics of the guest molecule on the anisotropic PES of the confining environment. In order to illustrate the power of the new methodology, in Ref. 29 we simulated the INS spectra of $para$-H_2 (p-H_2) and $ortho$-H_2 (o-H_2) in the small cage of the sII clathrate hydrate. The computed INS spectra were in remarkably good agreement with the experimental data.[6] They also revealed that almost every band in the experimental spectra is comprised of a multitude of distinct TR transitions, illustrating the pitfalls, and the near impossibility, of trying to assign the spectra correctly and with confidence by using overly simplified theoretical methods.

In Ref. 29, out of necessity, only a brief and rather superficial description of the methodology was given. The objective of this paper is to provide a complete account of our newly developed methodology for the computation of the INS spectra of an H_2 molecule in nanoconfinement. All the important steps in this technically demanding derivation are presented, and the often elaborate working expressions for the key matrix elements involving the 5D TR wave functions are obtained. We also describe the efficient procedure implemented by us recently, and utilized in Ref. 29, for the calculation of the 5D TR eigenstates in the very compact contracted basis, which are the essential ingredients for computing the INS spectra. This paper will serve as a reference in the future applications of this approach to other H_2-containing systems, and for the methodological extensions to entrapped polyatomic molecules such as CH_4.

II. THEORY

A. Basic equations

The starting point for our treatment of the INS spectra of the nanoconfined molecular hydrogen is the standard expression for the neutron scattering double differential cross section in the first Born approximation:[25,30]

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{k'}{k} S(\vec{\kappa}, \omega), \tag{1}$$

where

$$S(\vec{\kappa}, \omega) = \sum_i p_i \sum_f |M_f^i|^2 \delta[\omega - (\epsilon_f - \epsilon_i)/\hbar], \tag{2}$$

and

$$M_f^i = \sum_n \langle f|\hat{b}_n \exp(i\vec{\kappa}\cdot\vec{r}_n)|i\rangle. \tag{3}$$

In Eqs. (1)–(3), $|i\rangle$ stands for the initial state of the scattering molecular system with the energy ϵ_i, p_i is its statistical weight, $|f\rangle$ is the final state with the energy ϵ_f, $\vec{\kappa} = \vec{k} - \vec{k}'$, with $\vec{k}$ and $\vec{k}'$ the wave vectors of the incident and the scattered neutrons, respectively, $\hbar\omega = E - E' = \hbar^2(k^2 - k'^2)/(2m)$, with m the neutron mass, $\hat{b}_n$ is the scattering length operator, and $\vec{r}_n$ is the position of nucleus n. For a single proton n,

$$\hat{b}_n = b_1 + b_2 \frac{\vec{\sigma}}{2}\cdot\vec{i}_n, \tag{4}$$

where $\frac{\vec{\sigma}}{2}$ represents the neutron spin and $\vec{i}_n$ the nuclear spin of proton n; the coefficients b_1 and b_2 are discussed later.

When a single confined H_2 molecule is considered, the position vectors of its two hydrogen atoms can be written as

$$\vec{r}_n = \vec{R}_{c.m.} + \frac{(-1)^n}{2}\vec{\rho}, \qquad n = 1, 2 \tag{5}$$

$\vec{R}_{c.m.}$ being the position vector of the center of mass (c.m.) of H_2 and $\vec{\rho}$ the vector connecting the two H atoms. With the help of Eqs. (4) and (5), the expression for M_f^i in Eq. (3) becomes

$$
\begin{aligned}
M_f^i &= \sum_{n=1}^{2} \langle f|\hat{b}_n \exp(i\vec{\kappa}\cdot\vec{r}_n)|i\rangle, \\
&= \sum_{n=1}^{2} \langle f| \left(b_1 + b_2 \frac{\vec{\sigma}}{2}\cdot\vec{i}_n \right) \exp\left[i\vec{\kappa}\cdot\left(\vec{R}_{c.m.} + \frac{(-1)^n}{2}\vec{\rho}\right)\right] |i\rangle \\
&= \langle f|V_1 + V_2 + V_3|i\rangle,
\end{aligned}
\tag{6}
$$

where

$$
\begin{aligned}
V_1 &= 2b_1 \exp\left(i\vec{\kappa}\cdot\vec{R}_{c.m.}\right) \cos\left(\vec{\kappa}\cdot\vec{\rho}/2\right), \\
V_2 &= \frac{b_2}{2}\vec{\sigma}\cdot\left(\vec{i}_1 + \vec{i}_2\right) \exp\left(i\vec{\kappa}\cdot\vec{R}_{c.m.}\right) \cos\left(\vec{\kappa}\cdot\vec{\rho}/2\right), \\
V_3 &= i\frac{b_2}{2}\vec{\sigma}\cdot\left(\vec{i}_1 - \vec{i}_2\right) \exp\left(i\vec{\kappa}\cdot\vec{R}_{c.m.}\right) \sin\left(\vec{\kappa}\cdot\vec{\rho}/2\right).
\end{aligned}
\tag{7}
$$

For an H_2 molecule confined inside a cavity, the total wave functions of the initial ($|i\rangle$) and final states ($|f\rangle$) in Eqs. (1)–(3) can be written as the product of the nuclear-spin and spatial wave functions:

$$
\begin{aligned}
|i\rangle &= |I_i\rangle|\Psi_i^{5D}(\vec{R}_{c.m.}, \theta, \phi)\rangle, \\
|f\rangle &= |I_f\rangle|\Psi_f^{5D}(\vec{R}_{c.m.}, \theta, \phi)\rangle.
\end{aligned}
\tag{8}
$$

$|I_i\rangle$ and $|I_f\rangle$ stand for the initial- and final-state nuclear spin wave functions of H_2, respectively. I is the total nuclear spin of H_2 molecule, $I = 0$ for p-H_2, and $I = 1$ for o-H_2. For the spatial components of $|i\rangle$ and $|f\rangle$ we use the 5D eigenfunctions $|\Psi_\tau^{5D}(\vec{R}_{c.m.}, \theta, \phi)\rangle$ ($\tau = i, f$) of the 5D TR Hamiltonian for a rigid H_2 molecule inside a (rigid) nanocavity, associated with the corresponding TR energy levels ϵ_τ; θ, ϕ are the two angles specifying the direction of $\vec{\rho}$, i.e., the orientation of H_2 within the cavity. The TR Hamiltonian and our current computational methodology for accurate calculation of the 5D TR energy levels and wave functions $|\Psi_\tau^{5D}(\vec{R}_{c.m.}, \theta, \phi)\rangle$ using a compact product contracted basis are presented in Sec. II B. Hereafter, $|\Psi_\tau^{5D}(\vec{R}_{c.m.}, \theta, \phi)\rangle$ are denoted as $|\Psi_\tau^{5D}\rangle$, and are defined in Eq. (23).

Combining the product form of the initial and final states in Eq. (8) with the expressions for V_i ($i = 1 - 3$) in Eq. (7), M_f^i in Eq. (6) can be factorized as

$$
\begin{aligned}
M_f^i &= 2b_1 \delta_{I_f I_i} \left\langle \Psi_f^{5D} \left| \exp\left(i\vec{\kappa}\cdot\vec{R}_{c.m.}\right) \cos\left(\vec{\kappa}\cdot\vec{\rho}/2\right) \right| \Psi_i^{5D} \right\rangle \\
&\quad + \frac{b_2}{2} \left\langle I_f \left| \vec{\sigma}\cdot\left(\vec{i}_1 + \vec{i}_2\right) \right| I_i \right\rangle \left\langle \Psi_f^{5D} \left| \exp\left(i\vec{\kappa}\cdot\vec{R}_{c.m.}\right) \cos\left(\vec{\kappa}\cdot\vec{\rho}/2\right) \right| \Psi_i^{5D} \right\rangle \\
&\quad + i\frac{b_2}{2} \left\langle I_f \left| \vec{\sigma}\cdot\left(\vec{i}_1 - \vec{i}_2\right) \right| I_i \right\rangle \left\langle \Psi_f^{5D} \left| \exp\left(i\vec{\kappa}\cdot\vec{R}_{c.m.}\right) \sin\left(\vec{\kappa}\cdot\vec{\rho}/2\right) \right| \Psi_i^{5D} \right\rangle.
\end{aligned}
\tag{9}
$$

The above equation for M_f^i contains two types of matrix elements, (i) those which involve the nuclear-spin wave functions $|I_\tau\rangle$ $(\tau = i, f)$, and describe the coupling between the neutron spin and the nuclear spins of the two protons of H_2, and (ii) those involving the coupled 5D TR wave functions $|\Psi_\tau^{5D}\rangle$ $(\tau = i, f)$ of H_2 and the scattering vector $\vec{\kappa}$, which depend only on the spatial coordinates of the scattering system. These two types of matrix elements will be referred to as the spin and spatial matrix elements, respectively. The spatial matrix elements appearing in Eq. (9) are designated as P_{fi}^{5D} and Q_{fi}^{5D},

$$P_{fi}^{5D} \equiv \left\langle \Psi_f^{5D} \left| \exp\left(i\vec{\kappa}\cdot\vec{R}_{\text{c.m.}}\right) \cos\left(\vec{\kappa}\cdot\vec{\rho}/2\right) \right| \Psi_i^{5D} \right\rangle, \tag{10}$$

and

$$Q_{fi}^{5D} \equiv \left\langle \Psi_f^{5D} \left| \exp\left(i\vec{\kappa}\cdot\vec{R}_{\text{c.m.}}\right) \sin\left(\vec{\kappa}\cdot\vec{\rho}/2\right) \right| \Psi_i^{5D} \right\rangle. \tag{11}$$

It has long been recognized[31] that only the spin matrix element $\left\langle I_f \left| \vec{\sigma}\cdot\left(\vec{i}_1 - \vec{i}_2\right) \right| I_i \right\rangle$ in Eq. (9) couples the states of H_2 with different total nuclear spin I, i.e, $I_f \neq I_i$ (in fact it is zero for $I_f = I_i$), and therefore induces conversion between o- and p-H_2. This nuclear-spin term is associated with the spatial matrix element Q_{fi}^{5D} in Eq. (11). The spin matrix element $\left\langle I_f \left| \vec{\sigma}\cdot\left(\vec{i}_1 + \vec{i}_2\right) \right| I_i \right\rangle$ in Eq. (9), associated with P_{fi}^{5D} above, is zero when $I_f \neq I_i$,[27,30,32] and thus contributes only to the same-I transitions, p-$H_2 \to p$-H_2 and o-$H_2 \to o$-H_2. Consequently, one obtains the following general expression:

$$\left|M_f^i\right|^2 = \sigma_{I_i \to I_f} \times \begin{cases} \left|P_{fi}^{5D}\right|^2 & I_i = I_f \\ \\ \left|Q_{fi}^{5D}\right|^2 & I_i \neq I_f \end{cases} \tag{12}$$

In Eq. (12), $\sigma_{I_i \to I_f}$ are the neutron scattering cross sections for the total nuclear spin transitions $I_i \to I_f$, and the expressions for them are known.[27,30,32] For the unpolarized incident neutron beam, in terms of the coherent (σ_{coh}) and incoherent scattering cross sections (σ_{inc}) for the proton,[30] $\sigma_{I_i \to I_f}$ are given by

$$\sigma_{I_i \to I_f} = \begin{cases} 4\sigma_{coh} & 0 \to 0 \\ \\ 4\sigma_{coh} + \dfrac{8}{3}\sigma_{inc} & 1 \to 1 \\ \\ 4\sigma_{inc} & 0 \to 1 \\ \\ \dfrac{4}{3}\sigma_{inc} & 1 \to 0 \end{cases} \tag{13}$$

The values of the coherent and incoherent scattering cross sections for the proton are[33] $\sigma_{coh} = 1.76 \times 10^{-28}$ m^2 and $\sigma_{inc} = 80.26 \times 10^{-28}$ m^2. Clearly, σ_{inc} is much larger than σ_{coh}. For this reason p-$H_2 \to p$-H_2 ($J = 0 \to 0$) transition, which according to Eq. (13) is weighted by σ_{coh}, contributes little to the INS spectra of nanoconfined H_2, such as those of H_2 molecule in the clathrate hydrate cages.[6,29]

The spatial matrix elements P_{fi}^{5D} and Q_{fi}^{5D} in Eqs. (10)-(12) are evaluated in Sec. II C. But first we describe the computational approach employed to calculate the 5D TR eigenstates of the caged H_2 molecule, which serve as the INS initial and final states $|\Psi_\tau^{5D}\rangle$ $(\tau = i, f)$ in Eqs. (10) and (11) .

B. Calculation of the 5D translation-rotation eigenstates in a contracted basis

The methodology for computing the TR energy levels and wave functions utilized in this work, as well as in Ref. 29, has evolved in our group over a number of years. Recently[22] we have implemented the procedure for contracting the initial 5D direct-product basis which is both simpler and more efficient than the approach used previously. Effective basis set contraction is essential for the feasibilty of the quantum 5D bound-state calculations, and hence the calculation of the INS spectra. The new procedure was not documented previously, and because of its importance for our INS simulations, a full account is given here.

The host cage is taken to be rigid and the bond length of the diatomic guest molecule is held fixed. The five coordinates (x, y, z, θ, ϕ) are employed; x, y and z are the Cartesian coordinates of the c.m. of H_2, while the two polar angles θ and ϕ specify the orientation of H_2 relative to the cavity. The coordinate system is aligned with the three principal axes of the cage, and its origin is at the c.m. of the cage. The cage, whether formed by a molecule such as C_{60} or C_{70}, or a part of the 3D crystalline framework, as in clathrate hydrates or MOFs, is much heavier than the guest molecule; therefore, it can be safely treated as infinitely heavy and nonrotating. In this case, the 5D Hamiltonian for the TR motions of the caged diatomic molecule is[15]

$$H = -\frac{\hbar}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + B\mathbf{j}^2 + V(x, y, z, \theta, \phi), \tag{14}$$

where m is the mass of the guest molecule, while B and $\mathbf{j}^2$ are the rotational constant and angular momentum operator, respectively, of the diatomic. $V(x, y, z, \theta, \phi)$ is the 5D PES describing the intermolecular interaction between the guest molecule and the host cavity.

For the matrix representation of the TR Hamiltonian in Eq. (14), the 5D direct product basis $\{|X_\alpha\rangle|Y_\beta\rangle|Z_\gamma\rangle|jm\rangle\}$ is used.[34] $\{|X_\alpha\rangle|Y_\beta\rangle|Z_\gamma\rangle\}$ is the 3D direct product discrete variable representation (DVR)[35] basis in the x, y, z co-ordinates; it is labeled by the grid points $\{X_\alpha\}$, $\{Y_\beta\}$, and $\{Z_\gamma\}$, at which the respective DVR basis functions are localized. The dimensions of the 1D DVRs in x, y and z are N_x, N_y, and N_z, respectively. The modified spherical harmonics $\overline{Y}_{jm}(\mathbf{\Omega})$ constitute the $\{|jm\rangle\}$ basis in the angular coordinates $\mathbf{\Omega} = (\theta, \phi)$,[34]

$$|jm\rangle = \overline{Y}_{jm}(\mathbf{\Omega}) = (-1)^m P_{j,m}(\theta)F_m(\phi). \tag{15}$$

$\overline{Y}_{jm}(\mathbf{\Omega})$ are real functions, $P_{j,m}(\theta)$ are the normalized associated Legendre functions, and

$$F_m(\phi) = \begin{cases} \pi^{-1/2}\cos(m\phi) & m > 0 \\ (2\pi)^{-1/2} & m = 0 \\ \pi^{-1/2}\sin(m\phi) & m < 0. \end{cases} \tag{16}$$

The 5D direct-product basis $\{|X_\alpha\rangle|Y_\beta\rangle|Z_\gamma\rangle|jm\rangle\}$ easily becomes prohibitively large for the problem at hand. A very effective and fast method for the basis set contraction to which we resorted recently involves the diagonalization of matrices of the reduced-dimension Hamiltonians obtained from the full Hamiltonian operator by fixing certain coordinates at some reference values,[22,36,37] or averaging over them. In our present approach, the intermediate, purely translational reduced-dimension 3D Hamiltonian $^{3D}h^{xyz}$ is defined as

$$^{3D}h^{xyz} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + \overline{V}(x, y, z), \tag{17}$$

where $\overline{V}(x, y, z)$ is the full 5D PES in Eq. (14) averaged over the angular coordinates,

$$\overline{V}(x, y, z) = \frac{1}{4\pi}\int V(x, y, z, \mathbf{\Omega})d\mathbf{\Omega}. \tag{18}$$

Its eigenvalues and eigenvectors are obtained by diagonalizing it in the $\{|X_\alpha\rangle|Y_\beta\rangle|Z_\gamma\rangle\}$ basis,

$$^{3D}h^{xyz}|\Phi_t^{xyz}\rangle = {}^{3D}\epsilon_t^{xyz}|\Phi_t^{xyz}\rangle, \tag{19}$$

where

$$|\Phi_t^{xyz}\rangle = \sum_{q(\alpha\beta\gamma)=1}^{N_{xyz}} {}^{3D}C_{q(\alpha\beta\gamma),t}^{xyz}|X_\alpha\rangle|Y_\beta\rangle|Z_\gamma\rangle, \tag{20}$$

and $N_{xyz} = N_x \times N_y \times N_z$. In Eq. (20), the summation index $q(\alpha\beta\gamma)$ denotes that each of its values corresponds to one particular ordered triplet of the DVR indices α, β, γ. The number of eigenvectors $|\Phi_t^{xyz}\rangle$ which are kept in the final basis, denoted n_t^{xyz}, is *much smaller* than N_{xyz}, because the 3D eigenvectors $\{|\Phi_t^{xyz}\rangle\}$ already contain a significant portion of the solution of the full 5D problem. One could generate also a contracted angular basis consisting of the 2D hindered-rotor eigenvectors of the purely angular part of the Hamiltonian in Eq. (14). However, tests involving H_2 inside fullerenes, clathrate hydrates, and MOFs, showed that this was not necessary. Therefore, our final 5D product contracted basis consists of the contracted 3D translational basis functions $\{|\Phi_t^{xyz}\rangle\}$ and the 2D angular basis $\{|jm\rangle\}$.

In this 5D (partially) contracted basis $\{|\Phi_t^{xyz}\rangle|jm\rangle\}$, the matrix elements of the full 5D TR Hamiltonian in Eq. (14) are found to be

$$
\begin{aligned}
H_{tjm}^{t'j'm'} &= \delta_{tt'}\delta_{j'j}\delta_{m'm}\,{}^{3D}\epsilon_t^{xyz} - \delta_{j'j}\delta_{m'm}\sum_{q(\alpha\beta\gamma)=1}^{N_{xyz}}\,{}^{3D}C_{q(\alpha\beta\gamma),t'}^{xyz}\,\overline{V}(X_\alpha,Y_\beta,Z_\gamma)\,{}^{3D}C_{q(\alpha\beta\gamma),t}^{xyz} \\
&+ \delta_{tt'}\delta_{j'j}\delta_{m'm}Bj(j+1)\hbar^2 \\
&+ \sum_{q(\alpha\beta\gamma)=1}^{N_{xyz}}\,{}^{3D}C_{q(\alpha\beta\gamma),t'}^{xyz}\,{}^{3D}C_{q(\alpha\beta\gamma),t}^{xyz}\langle j'm'\mid V(X_\alpha,Y_\beta,Z_\gamma,\boldsymbol{\Omega})\mid jm\rangle.
\end{aligned}
\tag{21}
$$

The dimension of this final Hamiltonian matrix, denoted N^{5D}, is $n_t^{xyz}\times(j_{\max}+1)^2$. Its diagonalization yields the TR energy levels ϵ_i^{5D} and the corresponding 5D TR eigenvectors $|\Psi_i^{5D}\rangle$. The latter are expanded in the product contracted basis $\{|\Phi_t^{xyz}\rangle|jm\rangle\}$ as

$$
|\Psi_i^{5D}\rangle = \sum_{\mathbf{p}(tjm)=1}^{N^{5D}}\,{}^{5D}W_{\mathbf{p}(tjm),i}^{xyz\theta\phi}|\Phi_t^{xyz}\rangle|jm\rangle,
\tag{22}
$$

where $\mathbf{p}$ is the index of the (real) coefficients ${}^{5D}W_{\mathbf{p}(tjm),i}^{xyz\theta\phi}$; it is a direct product of the indices t and jm. The actual calculations of the INS spectra require the expansion coefficients $\{{}^{5D}A_{\alpha\beta\gamma jm,i}^{xyz\theta\phi}\}$ of $|\Psi_i^{5D}\rangle$ in the initial uncontracted basis $\{|X_\alpha\rangle|Y_\beta\rangle|Z_\gamma\rangle|jm\rangle\}$. They are obtained by combining Eq. (22) with Eq. (20),

$$
\begin{aligned}
|\Psi_i^{5D}\rangle &= \sum_{\mathbf{p}(tjm)=1}^{N^{5D}}\,{}^{5D}W_{\mathbf{p}(tjm),i}^{xyz\theta\phi}|\Phi_t^{xyz}\rangle|jm\rangle \\
&= \sum_{\mathbf{p}(tjm)=1}^{N^{5D}}\,{}^{5D}W_{\mathbf{p}(tjm),i}^{xyz\theta\phi}\sum_{q(\alpha\beta\gamma)=1}^{N_{xyz}}\,{}^{3D}C_{q(\alpha\beta\gamma),t}^{xyz}|X_\alpha\rangle|Y_\beta\rangle|Z_\gamma\rangle|jm\rangle \\
&= \sum_{(jm)=1}^{(j_{max}+1)^2}\sum_{q(\alpha\beta\gamma)=1}^{N_{xyz}}\left(\sum_{t=1}^{n_t^{xyz}}\,{}^{5D}W_{\mathbf{p}(tjm),i}^{xyz\theta\phi}\,{}^{3D}C_{q(\alpha\beta\gamma),t}^{xyz}\right)|X_\alpha\rangle|Y_\beta\rangle|Z_\gamma\rangle|jm\rangle \\
&= \sum_{(jm)=1}^{(j_{max}+1)^2}\sum_{q(\alpha\beta\gamma)=1}^{N_{xyz}}\,{}^{5D}A_{\alpha\beta\gamma jm,i}^{xyz\theta\phi}|X_\alpha\rangle|Y_\beta\rangle|Z_\gamma\rangle|jm\rangle \\
&= \sum_{\alpha\beta\gamma jm}\,{}^{5D}A_{\alpha\beta\gamma jm,i}^{xyz\theta\phi}|X_\alpha\rangle|Y_\beta\rangle|Z_\gamma\rangle|jm\rangle.
\end{aligned}
\tag{23}
$$

The expansion of $|\Psi_i^{5D}\rangle$ in the last line of Eq. (23) is used to compute the spatial matrix elements P_{fi}^{5D} and Q_{fi}^{5D} in Eqs. (10) and (11), as shown below.

C. Evaluation of the spatial matrix elements

1. The translational component

Let the two angles $(\theta_{\vec{\kappa}},\phi_{\vec{\kappa}})$ define the direction of $\vec{\kappa}$, and $\kappa\equiv|\vec{\kappa}|$. The three Cartesian components of $\vec{\kappa}$ are

$$
\begin{aligned}
\kappa_x &= \kappa\sin\theta_{\vec{\kappa}}\cos\phi_{\vec{\kappa}}, \\
\kappa_y &= \kappa\sin\theta_{\vec{\kappa}}\sin\phi_{\vec{\kappa}}, \\
\kappa_z &= \kappa\cos\theta_{\vec{\kappa}}.
\end{aligned}
\tag{24}
$$

In addition, let $(X_{\text{c.m.}},Y_{\text{c.m.}},Z_{\text{c.m.}})$ be the three components of $\vec{R}_{\text{c.m.}}$. With this, P_{fi}^{5D} and Q_{fi}^{5D} in Eqs. (10) and (11) can be written as

$$
\begin{aligned}
P_{fi}^{5D} &= \left\langle\Psi_f^{5D}\left|\exp\left[i\left(\kappa_x X_{\text{c.m.}}+\kappa_y Y_{\text{c.m.}}+\kappa_z Z_{\text{c.m.}}\right)\right]\cos\left(\vec{\kappa}\cdot\vec{\rho}/2\right)\right|\Psi_i^{5D}\right\rangle, \\
Q_{fi}^{5D} &= \left\langle\Psi_f^{5D}\left|\exp\left[i\left(\kappa_x X_{\text{c.m.}}+\kappa_y Y_{\text{c.m.}}+\kappa_z Z_{\text{c.m.}}\right)\right]\sin\left(\vec{\kappa}\cdot\vec{\rho}/2\right)\right|\Psi_i^{5D}\right\rangle,
\end{aligned}
\tag{25}
$$

where κ_x, κ_y, and κ_z are defined in Eq. (24). Expanding $|\Psi_i^{5D}\rangle$ and $|\Psi_f^{5D}\rangle$ in the basis $\{|X_\alpha\rangle|Y_\beta\rangle|Z_\gamma\rangle|jm\rangle\}$, as in Eq. (23), P_{fi}^{5D} in Eq. (25) becomes

$$
\begin{aligned}
P_{fi}^{5D} & = \sum_{\alpha'\beta'\gamma'j'm'\alpha\beta\gamma jm} {}^{5D}A_{\alpha'\beta'\gamma'j'm',f}^{xyz\theta\phi}\,{}^{5D}A_{\alpha\beta\gamma jm,i}^{xyz\theta\phi}\langle X_{\alpha'}|\exp\left(i\kappa_x X_{\mathrm{c.m.}}\right)|X_\alpha\rangle \\
& \times \langle Y_{\beta'}|\exp\left(i\kappa_y Y_{\mathrm{c.m.}}\right)|Y_\beta\rangle\langle Z_{\gamma'}|\exp\left(i\kappa_z Z_{\mathrm{c.m.}}\right)|Z_\gamma\rangle \\
& \times \langle j'm'|\cos\left(\vec{\kappa}\cdot\vec{\rho}/2\right)|jm\rangle.
\end{aligned}
\tag{26}
$$

In the same way, an expression identical to Eq. (26) is obtained for Q_{fi}^{5D} in Eq. (25), except that the matrix element $\langle j'm'|\cos\left(\vec{\kappa}\cdot\vec{\rho}/2\right)|jm\rangle$ is replaced with $\langle j'm'|\sin\left(\vec{\kappa}\cdot\vec{\rho}/2\right)|jm\rangle$. Eq. (26), and the analogous expression for Q_{fi}^{5D}, seems rather forbidding and extremely costly to evaluate, since it involves the summation over ten indices. Fortunately, these equations can be greatly simplified, and the computational effort of their evaluation drastically reduced, by exploiting one of the chief advantages of the DVR - that to a high degree of accuracy, the matrices of coordinate operators are diagonal in the DVR, their matrix elements being simply the values of the coordinate operator at the DVR points.[38,39] Thus,

$$
\begin{aligned}
\langle X_{\alpha'}|\exp\left(i\kappa_x X_{\mathrm{c.m.}}\right)|X_\alpha\rangle & = \exp\left(i\kappa_x X_\alpha\right)\delta_{\alpha'\alpha}, \\
\langle Y_{\beta'}|\exp\left(i\kappa_y Y_{\mathrm{c.m.}}\right)|Y_\beta\rangle & = \exp\left(i\kappa_y Y_\beta\right)\delta_{\beta'\beta}, \\
\langle Z_{\gamma'}|\exp\left(i\kappa_z Z_{\mathrm{c.m.}}\right)|Z_\gamma\rangle & = \exp\left(i\kappa_z Z_\gamma\right)\delta_{\gamma'\gamma}.
\end{aligned}
\tag{27}
$$

With this, the expressions for P_{fi}^{5D} and Q_{fi}^{5D} take a considerably simpler form,

$$
\begin{aligned}
P_{fi}^{5D} & = \sum_{\alpha\beta\gamma jmj'm'} {}^{5D}A_{\alpha\beta\gamma j'm',f}^{xyz\theta\phi}\,{}^{5D}A_{\alpha\beta\gamma jm,i}^{xyz\theta\phi}\exp\left[i\left(\kappa_x X_\alpha + \kappa_y Y_\beta + \kappa_z Z_\gamma\right)\right] \\
& \times \langle j'm'|\cos\left(\vec{\kappa}\cdot\vec{\rho}/2\right)|jm\rangle,
\end{aligned}
\tag{28}
$$

and

$$
\begin{aligned}
Q_{fi}^{5D} & = \sum_{\alpha\beta\gamma jmj'm'} {}^{5D}A_{\alpha\beta\gamma j'm',f}^{xyz\theta\phi}\,{}^{5D}A_{\alpha\beta\gamma jm,i}^{xyz\theta\phi}\exp\left[i\left(\kappa_x X_\alpha + \kappa_y Y_\beta + \kappa_z Z_\gamma\right)\right] \\
& \times \langle j'm'|\sin\left(\vec{\kappa}\cdot\vec{\rho}/2\right)|jm\rangle,
\end{aligned}
\tag{29}
$$

with κ_x, κ_y, and κ_z defined in Eq. (24). The use of the 3D direct product DVR $\{|X_\alpha\rangle|Y_\beta\rangle|Z_\gamma\rangle\}$ basis for the H_2 c.m. translational degrees of freedom, and in the expansion of $|\Psi_\tau^{5D}\rangle$ $(\tau = i, f)$ in Eq. (23), is crucial for the efficient computation of P_{fi}^{5D} and Q_{fi}^{5D}. Eqs. (28) and (29) provide the working expressions for the translational parts of P_{fi}^{5D} and Q_{fi}^{5D}, respectively.

2. The angular component

The last remaining step in the evaluation of P_{fi}^{5D} and Q_{fi}^{5D} is to derive the expressions for the angular matrix elements $\langle j'm'|\cos\left(\vec{\kappa}\cdot\vec{\rho}/2\right)|jm\rangle$ in Eq. (28) and $\langle j'm'|\sin\left(\vec{\kappa}\cdot\vec{\rho}/2\right)|jm\rangle$ in Eq. (29). For this purpose, it is necessary to express both $\cos\left(\vec{\kappa}\cdot\vec{\rho}/2\right)$ and $\sin\left(\vec{\kappa}\cdot\vec{\rho}/2\right)$ in terms of the functions $\overline{Y}_{jm}(\theta,\phi)$ of Eq. (15). The angles (θ,ϕ) are associated with $\vec{\rho}$ (along the H_2 bond), while the direction of $\vec{\kappa}$ is defined by $(\theta_{\vec{\kappa}}, \phi_{\vec{\kappa}})$. We use the well known expression[40]

$$
\exp\left(i\vec{\kappa}\cdot\vec{\rho}/2\right) = \sum_{lm} i^l 4\pi j_l\left(\kappa\rho/2\right)Y_{lm}^*(\theta_{\vec{\kappa}}, \phi_{\vec{\kappa}})Y_{lm}(\theta,\phi),
\tag{30}
$$

where $\kappa \equiv |\vec{\kappa}|$, $\rho \equiv |\vec{\rho}|$, and $j_l\left(\kappa\rho/2\right)$ are the spherical Bessel functions.[41] For the standard spherical harmonics $Y_{lm}(\theta,\phi)$,

$$
Y_{lm}^*(\theta,\phi) = (-1)^m Y_{l,-m}(\theta,\phi).
\tag{31}
$$

Given the definition of $\overline{Y}_{lm}(\theta, \phi)$ in Eqs. (15) and (16), they are related to $Y_{lm}(\theta, \phi)$ in the following way:

$$
\overline{Y}_{lm}(\theta, \phi) = \begin{cases} \dfrac{1}{\sqrt{2}} \left[Y_{lm}(\theta, \phi) + Y_{l,m}^*(\theta, \phi) \right] & m > 0 \\[3mm] Y_{l0}(\theta, \phi) & m = 0 \\[3mm] \dfrac{1}{i\sqrt{2}} \left[Y_{lm}(\theta, \phi) - Y_{l,m}^*(\theta, \phi) \right] & m < 0. \end{cases}
\tag{32}
$$

Based on the above, one readily derives the following equation:

$$
\sum_m Y_{lm}^*(\theta_{\vec{\kappa}}, \phi_{\vec{\kappa}}) Y_{lm}(\theta, \phi) = \sum_m \overline{Y}_{lm}(\theta_{\vec{\kappa}}, \phi_{\vec{\kappa}}) \overline{Y}_{lm}(\theta, \phi).
\tag{33}
$$

Splitting Eq. (30) into real and imaginary parts and taking into account Eq. (33), we get

$$
\cos\left(\vec{\kappa} \cdot \vec{\rho}/2\right) = Re\left[\sum_l \left(i^l 4\pi j_l\left(\kappa\rho/2\right) \sum_m \overline{Y}_{lm}(\theta_{\vec{\kappa}}, \phi_{\vec{\kappa}}) \overline{Y}_{lm}(\theta, \phi) \right) \right],
$$
$$
\sin\left(\vec{\kappa} \cdot \vec{\rho}/2\right) = Im\left[\sum_l \left(i^l 4\pi j_l\left(\kappa\rho/2\right) \sum_m \overline{Y}_{lm}(\theta_{\vec{\kappa}}, \phi_{\vec{\kappa}}) \overline{Y}_{lm}(\theta, \phi) \right) \right].
\tag{34}
$$

Utilizing Eq. (34) we can compute $\langle j'm' | \cos\left(\vec{\kappa} \cdot \vec{\rho}/2\right) | jm \rangle$ and $\langle j'm' | \sin\left(\vec{\kappa} \cdot \vec{\rho}/2\right) | jm \rangle$ in Eqs. (28) and (29), respectively. This requires the evaluation of the matrix elements designated as $\widetilde{\mathbb{I}}_{m'Mm}^{j'Lj}$:

$$
\widetilde{\mathbb{I}}_{m'Mm}^{j'Lj} \equiv \int d\mathbf{\Omega}\, \overline{Y}_{j'm'}(\theta, \phi) \overline{Y}_{LM}(\theta, \phi) \overline{Y}_{jm}(\theta, \phi),
\tag{35}
$$

where $\mathbf{\Omega} = (\theta, \phi)$. $\widetilde{\mathbb{I}}_{m'Mm}^{j'Lj}$ is obviously real, since the integration is over the product of three real functions. To compute $\widetilde{\mathbb{I}}_{m'Mm}^{j'Lj}$, because of the relationship between $\overline{Y}_{lm}(\theta, \phi)$ and $Y_{lm}(\theta, \phi)$ in Eq. (32), it is necessary to evaluate first the matrix elements

$$
\mathbb{I}_{m'Mm}^{j'Lj} \equiv \langle j'm' | Y_{LM}(\theta, \phi) | jm \rangle = \int d\mathbf{\Omega}\, \overline{Y}_{j'm'}(\theta, \phi) Y_{LM}(\theta, \phi) \overline{Y}_{jm}(\theta, \phi)
\tag{36}
$$

and

$$
\mathbb{I}^{\dagger}{}_{m'Mm}^{j'Lj} \equiv \langle j'm' | Y_{LM}^*(\theta, \phi) | jm \rangle = (-1)^M \int d\mathbf{\Omega}\, \overline{Y}_{j'm'}(\theta, \phi) Y_{L-M}(\theta, \phi) \overline{Y}_{jm}(\theta, \phi).
\tag{37}
$$

We begin with $\mathbb{I}_{m'Mm}^{j'Lj}$ in Eq. (36). For this we use the well known expression for the integral over the product over three spherical harmonics,[42]

$$
\int d\mathbf{\Omega}\, Y_{J_3 M_3}(\theta, \phi) Y_{J_2 M_2}(\theta, \phi) Y_{J_1 M_1}(\theta, \phi) = \left[\frac{(2J_1 + 1)(2J_2 + 1)(2J_3 + 1)}{4\pi} \right]^{\frac{1}{2}}
$$
$$
\times \begin{pmatrix} J_1 & J_2 & J_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} J_1 & J_2 & J_3 \\ M_1 & M_2 & M_3 \end{pmatrix}.
\tag{38}
$$

In view of Eq. (38), it is useful to write Eq. (36) as

$$
\mathbb{I}_{m'Mm}^{j'Lj} = \mathbb{C}(j', L, j) \times \mathbb{G} \begin{pmatrix} j' & L & j \\ m' & M & m \end{pmatrix},
\tag{39}
$$

where

$$
\mathbb{C} \equiv \frac{1}{2} \left[\frac{(2j' + 1)(2L + 1)(2j + 1)}{4\pi} \right]^{\frac{1}{2}} \begin{pmatrix} j' & L & j \\ 0 & 0 & 0 \end{pmatrix}.
\tag{40}
$$

For $\mathbb{G}$ in Eq. (39), nine expressions are obtained for the different combinations of the relative signs and values of m' and m; they are given in Eqs. (A1)-(A9) of Appendix A.

$\mathbb{I}^{\dagger j' L j}_{m' M m}$ in Eq. (37) can be written, analogously to Eq. (39), as:

$$\mathbb{I}^{\dagger j' L j}_{m' M m} = (-1)^M \mathbb{C}(j', L, j) \times \mathbb{G} \begin{pmatrix} j' & L & j \\ m' & -M & m \end{pmatrix}. \tag{41}$$

With the expressions for $\mathbb{I}^{j' L j}_{m' M m}$ and $\mathbb{I}^{\dagger j' L j}_{m' M m}$ at hand, the key angular matrix element $\widetilde{\mathbb{I}}^{j' L j}_{m' M m}$ in Eq. (35) is given by

$$\widetilde{\mathbb{I}}^{j' L j}_{m' M m} = \mathbb{C}(j', L, j) \times \begin{cases} \dfrac{1}{\sqrt{2}} \left[\mathbb{G} \begin{pmatrix} j' & L & j \\ m' & M & m \end{pmatrix} + (-1)^M \mathbb{G} \begin{pmatrix} j' & L & j \\ m' & -M & m \end{pmatrix} \right] & M > 0 \\[2em] \mathbb{G} \begin{pmatrix} j' & L & j \\ m' & 0 & m \end{pmatrix} & M = 0 \\[2em] \dfrac{1}{i\sqrt{2}} \left[\mathbb{G} \begin{pmatrix} j' & L & j \\ m' & M & m \end{pmatrix} - (-1)^M \mathbb{G} \begin{pmatrix} j' & L & j \\ m' & -M & m \end{pmatrix} \right] & M < 0. \end{cases} \tag{42}$$

Due to the fact that $j' + L + j$ must be even for $\mathbb{C}(j', L, j)$ to be non-zero, the combined $\mathbb{G}$ terms in Eq. (42) following $\mathbb{C}(j', L, j)$ can be written in a somewhat simpler form given by Eqs. (B1)-(B3) in Appendix B.

By combining the expressions for $\widetilde{\mathbb{I}}^{j' L j}_{m' M m}$ in Eqs. (35) and (42) with Eq. (34) one obtains the following equations for the angular matrix elements in Eqs. (28) and (29),

$$\begin{aligned} \langle j' m' | \cos(\vec{\kappa} \cdot \vec{\rho}/2) | j m \rangle &= Re \left[\sum_L \left(i^L 4\pi j_L \left(\frac{\kappa\rho}{2} \right) \sum_M \widetilde{\mathbb{I}}^{j' L j}_{m' M m} \overline{Y}_{LM}(\theta_{\vec{\kappa}}, \phi_{\vec{\kappa}}) \right) \right] \quad L \equiv 2l \\ &= \sum_{l=0} \left((-1)^l 4\pi j_{2l} \left(\frac{\kappa\rho}{2} \right) \sum_{M=-2l}^{2l} \widetilde{\mathbb{I}}^{j' (2l) j}_{m' M m} \overline{Y}_{2l,M}(\theta_{\vec{\kappa}}, \phi_{\vec{\kappa}}) \right) \\[1.5em] \langle j' m' | \sin(\vec{\kappa} \cdot \vec{\rho}/2) | j m \rangle &= Im \left[\sum_L \left(i^L 4\pi j_L \left(\frac{\kappa\rho}{2} \right) \sum_M \widetilde{\mathbb{I}}^{j' L j}_{m' M m} \overline{Y}_{LM}(\theta_{\vec{\kappa}}, \phi_{\vec{\kappa}}) \right) \right] \quad L \equiv 2l+1 \\ &= \sum_{l=0} \left((-1)^l 4\pi j_{2l+1} \left(\frac{\kappa\rho}{2} \right) \sum_{M=-(2l+1)}^{2l+1} \widetilde{\mathbb{I}}^{j' (2l+1) j}_{m' M m} \overline{Y}_{2l+1,M}(\theta_{\vec{\kappa}}, \phi_{\vec{\kappa}}) \right). \end{aligned} \tag{43}$$

With this, P^{5D}_{fi} and Q^{5D}_{fi} in Eqs. (28) and (29), respectively, acquire their final form, in which they can be computed efficiently. Eqs. (12), (13), (28), (29), (42), and (43), combined together allow us to calculate the INS spectra of an H_2 molecule inside a nanocavity, i.e., the intensities of the INS transitions between the different initial and final TR states, using the coupled 5D TR wave functions of the confined H_2.

D.   Statistical weights of the initial states

To calculate the INS spectra it is necessary to know the statistical weights p_i in Eq. (2) of the initial states of the transitions. We consider a nanocavity with either a single p-H_2 or o-H_2 molecule inside. The two spin isomers are generally not in thermal equilibrium at low temperatures, and their relative concentrations in the material under study can vary, depending on the conditions of the sample preparation; there is no spontaneous interconversion between o-H_2 and p-H_2 on the time scale of the INS measurements. The population of the initial states, rotational and translational, of the guest molecule, p-H_2 or o-H_2, in the cavity is assumed to be thermal, weighted by the Boltzmann distribution at the temperature considered. Thus, $\{p_i\}$ can be determined for any temperature of interest. The INS spectra are often measured at very low temperatures, at which only the lowest rotational levels, $J = 0$ for p-H_2 and $J = 1$ for o-H_2, in the ground translational state are populated. Under these conditions, for p-H_2 only one initial state, the $J = 0$ rotational level, needs to be taken into account for the computation of the INS spectra. The situation is different for o-H_2. In most host materials its $J = 1$ level is split by the angular anisotropy of the PES into three components,[6,15,16] and the INS transitions originate from each of them. Let the energies of the three $J = 1$ sublevels

be E_0, E_1, and E_2, with E_0 being the ground state of o-H_2. In addition, let $\Delta E_1 = E_1 - E_0$ and $\Delta E_2 = E_2 - E_0$. Then the relative populations p_0, p_1, and p_2, of these three initial states of o-H_2 at the temperature T are given by

$$p_0 = \frac{1}{1 + \exp(-\beta \Delta E_1) + \exp(-\beta \Delta E_2)},$$

$$p_1 = \frac{\exp(-\beta \Delta E_1)}{1 + \exp(-\beta \Delta E_1) + \exp(-\beta \Delta E_2)}, \tag{44}$$

$$p_2 = \frac{\exp(-\beta \Delta E_2)}{1 + \exp(-\beta \Delta E_1) + \exp(-\beta \Delta E_2)},$$

where $\beta = (k_B T)^{-1}$ and k_B is the Boltzmann constant. In the case of o-H_2 in the small cage of clathrate hydrate, ΔE_1 and ΔE_2 are known both from the calculations[16] and the experiment.[6]

E.   Averaging the INS spectra over the random orientations of the nanocages

The experimental INS spectra of nanoconfined molecular hydrogen, e.g. H_2 in clathrate hydrates[6] and inside C_{60},[4] are typically taken from powdered samples, in which the nanocavities are randomly oriented. Hence, in order to achieve a more realistic and definitive comparison with the experimental data, the INS spectra computed as described above are averaged over all possible orientations of the nanocages. We choose the direction of the wave vector $\vec{k}$ of the incident neutron to define the z axis of the space-fixed frame of reference. The random orientations of the cages within this frame translate into random directions the scattering vector $\vec{\kappa}$, defined by the angles $(\theta_{\vec{\kappa}}, \phi_{\vec{\kappa}})$. The theoretical INS spectrum depends explicitly on $(\theta_{\vec{\kappa}}, \phi_{\vec{\kappa}})$, since these appear in the translational component of the spatial matrix elements P_{fi}^{5D} and Q_{fi}^{5D} through Eqs. (24), (28), and (29), and also in their angular component, through Eq. (43). A uniform $\{\theta_{\vec{\kappa}}, \phi_{\vec{\kappa}}\}$ grid, covering the entire range of these two angles, is chosen. Then, the INS spectrum is calculated separately for each $(\theta_{\vec{\kappa}}, \phi_{\vec{\kappa}})$ pair in the grid and the results are added up. This procedure yields the simulated INS spectrum of H_2 in randomly oriented nanocavities.

III.   CONCLUSIONS

We have presented a comprehensive description of the methodology introduced by us recently[29] for the quantum calculation of the INS spectra of an H_2 molecule confined inside a nanocavity. The main distinguishing feature of our approach is that it utilizes the rigorously calculated 5D TR energy levels and wave functions of the guest molecule as the initial and the final states of the INS transitions. Their implementation within the quantum INS formalism is novel and nontrivial, and is therefore described in detail. Integral and indispensable component of this methodology is the computational scheme also described in this paper, for computing the required 5D TR eigenstates very efficiently and in the form which greatly facilitates the subsequent evaluation of the key matrix elements needed in the calculation of the INS spectra. We are now able to compute accurately the INS spectra of the nanoconfined H_2, directly from the 5D intermolecular PES of the caged molecule and its coupled TR eigenstates. Since the TR coupling is treated in full, the INS spectra from the quantum simulations are exceptionally realistic and rich in details, and embody the complex quantum TR dynamics. Consequently, direct comparison is possible between the computed and experimental INS spectra, allowing a detailed interpretation and assignment of the latter, and providing a very stringent test of the quality of the 5D PES employed.

The performance of our methodology was already demonstrated successfully in Ref. 29, where the INS spectra of p-H_2 and o-H_2 in the small cage of the sII clathrate hydrate were computed and compared to the experimental spectra. Further more in-depth applications of the methodology described in this paper to the INS spectra of HD in the small cage of sII clathrate hydrate,[6] H_2 and HD in the fullerenes C_{60},[4] ATOCF,[3] and C_{70}, and in HKUST-1,[10] are in progress and the results will be reported in the near future. We intend to generalize our approach to enable the calculation of the INS spectra of nanoconfined polyatomic molecules. CH_4 is of special interest in this context, and we have already calculated its 6D TR eigenstates in methane hydrate.[36]

ACKNOWLEDGMENTS

Appendix A: Expressions for $\mathbb{G}$ in Eq. (39)

The expressions for $\mathbb{G}$, for the different combinations of the relative signs and values of m' and m:

$$(-1)^{m'} \begin{pmatrix} j' & L & j \\ -m' & M & m \end{pmatrix} + \begin{pmatrix} j' & L & j \\ m' & M & m \end{pmatrix} + (-1)^{m'+m} \begin{pmatrix} j' & L & j \\ -m' & M & -m \end{pmatrix}$$
$$+ (-1)^{m} \begin{pmatrix} j' & L & j \\ m' & M & -m \end{pmatrix} \qquad m' > 0 \quad m > 0, \tag{A1}$$

$$\sqrt{2} \left[(-1)^{m'} \begin{pmatrix} j' & L & j \\ -m' & M & 0 \end{pmatrix} + \begin{pmatrix} j' & L & j \\ m' & M & 0 \end{pmatrix} \right] \qquad m' > 0 \quad m = 0, \tag{A2}$$

$$-i(-1)^{m'} \begin{pmatrix} j' & L & j \\ -m' & M & m \end{pmatrix} - i \begin{pmatrix} j' & L & j \\ m' & M & m \end{pmatrix} + i(-1)^{m'+m} \begin{pmatrix} j' & L & j \\ -m' & M & -m \end{pmatrix}$$
$$+ i(-1)^{m} \begin{pmatrix} j' & L & j \\ m' & M & -m \end{pmatrix} \qquad m' > 0 \quad m < 0, \tag{A3}$$

$$\sqrt{2} \left[\begin{pmatrix} j' & L & j \\ 0 & M & m \end{pmatrix} + (-1)^{m} \begin{pmatrix} j' & L & j \\ 0 & M & -m \end{pmatrix} \right] \qquad m' = 0 \quad m > 0, \tag{A4}$$

$$2 \begin{pmatrix} j' & L & j \\ 0 & M & 0 \end{pmatrix} \qquad m' = 0 \quad m = 0, \tag{A5}$$

$$-i\sqrt{2} \left[\begin{pmatrix} j' & L & j \\ 0 & M & m \end{pmatrix} - (-1)^{m} \begin{pmatrix} j' & L & j \\ 0 & M & -m \end{pmatrix} \right] \qquad m' = 0 \quad m < 0, \tag{A6}$$

$$i(-1)^{m'} \begin{pmatrix} j' & L & j \\ -m' & M & m \end{pmatrix} - i \begin{pmatrix} j' & L & j \\ m' & M & m \end{pmatrix} + i(-1)^{m'+m} \begin{pmatrix} j' & L & j \\ -m' & M & -m \end{pmatrix}$$
$$- i(-1)^{m} \begin{pmatrix} j' & L & j \\ m' & M & -m \end{pmatrix} \qquad m' < 0 \quad m > 0, \tag{A7}$$

$$i\sqrt{2} \left[(-1)^{m'} \begin{pmatrix} j' & L & j \\ -m' & M & 0 \end{pmatrix} - \begin{pmatrix} j' & L & j \\ m' & M & 0 \end{pmatrix} \right] \qquad m' < 0 \quad m = 0, \tag{A8}$$

$$(-1)^{m'} \begin{pmatrix} j' & L & j \\ -m' & M & m \end{pmatrix} - \begin{pmatrix} j' & L & j \\ m' & M & m \end{pmatrix} - (-1)^{m'+m} \begin{pmatrix} j' & L & j \\ -m' & M & -m \end{pmatrix}$$
$$+ (-1)^{m} \begin{pmatrix} j' & L & j \\ m' & M & -m \end{pmatrix} \qquad m' < 0 \quad m < 0. \tag{A9}$$

Appendix B: Expressions for the combined $\mathbb{G}$ terms in Eq. (42)

$M > 0$

$$
\begin{cases}
\sqrt{2}(-1)^{m'}\begin{pmatrix} j' & L & j \\ -m' & M & m \end{pmatrix} + \sqrt{2}(-1)^{M}\begin{pmatrix} j' & L & j \\ -m' & M & -m \end{pmatrix} \\
+\sqrt{2}(-1)^{m}\begin{pmatrix} j' & L & j \\ m' & M & -m \end{pmatrix} & m' > 0 \quad m > 0, \\[3ex]
2(-1)^{m'}\begin{pmatrix} j' & L & j \\ -m' & M & 0 \end{pmatrix} & m' > 0 \quad m = 0, \\[3ex]
2(-1)^{m}\begin{pmatrix} j' & L & j \\ 0 & M & -m \end{pmatrix} & m' = 0 \quad m > 0, \\[3ex]
\sqrt{2}\left[(-1)^{m'}\begin{pmatrix} j' & L & j \\ -m' & M & m \end{pmatrix} - \begin{pmatrix} j' & L & j \\ m' & M & m \end{pmatrix} + (-1)^{m}\begin{pmatrix} j' & L & j \\ m' & M & -m \end{pmatrix}\right] & m' < 0 \quad m < 0, \\[3ex]
0 & \text{other } m',m \text{ combinations.}
\end{cases}
\tag{B1}
$$

$M = 0$

$$
\begin{cases}
2(-1)^{m'}\begin{pmatrix} j' & L & j \\ -m' & 0 & m \end{pmatrix} & m' > 0 \quad m > 0, \\[3ex]
2\begin{pmatrix} j' & L & j \\ 0 & 0 & 0 \end{pmatrix} & m' = 0 \quad m = 0, \\[3ex]
2(-1)^{m'}\begin{pmatrix} j' & L & j \\ -m' & 0 & m \end{pmatrix} & m' < 0 \quad m < 0, \\[3ex]
0 & \text{other } m',m \text{ combinations.}
\end{cases}
\tag{B2}
$$

$M < 0$

$$
\begin{cases}
\sqrt{2}(-1)^{M}\begin{pmatrix} j' & L & j \\ -m' & M & -m \end{pmatrix} - \sqrt{2}\begin{pmatrix} j' & L & j \\ m' & M & m \end{pmatrix} \\
+\sqrt{2}(-1)^{m}\begin{pmatrix} j' & L & j \\ m' & M & -m \end{pmatrix} & m' > 0 \quad m < 0, \\[3ex]
2(-1)^{m}\begin{pmatrix} j' & L & j \\ 0 & M & -m \end{pmatrix} & m' = 0 \quad m < 0, \\[3ex]
\sqrt{2}(-1)^{M}\begin{pmatrix} j' & L & j \\ -m' & M & -m \end{pmatrix} - \sqrt{2}\begin{pmatrix} j' & L & j \\ m' & M & m \end{pmatrix} \\
+\sqrt{2}(-1)^{m'}\begin{pmatrix} j' & L & j \\ -m' & M & m \end{pmatrix} & m' < 0 \quad m > 0, \\[3ex]
2(-1)^{m'}\begin{pmatrix} j' & L & j \\ -m' & M & 0 \end{pmatrix} & m' < 0 \quad m = 0, \\[3ex]
0 & \text{other } m',m \text{ combinations.}
\end{cases}
\tag{B3}
$$

[1] A. J. Ramirez-Cuesta, M. J. Jones and W. I. F. David, Materials Today **12**, (11) 54 (2009).

[2] G. J. Kearley and M. R. Johnson, Vib. Spectrosc. **53**, 54 (2010).

[3] A. J. Horsewill, K. S. Panesar, S. Rols, M. R. Johnson, Y. Murata, K. Komatsu, S. Mamone, A. Danquigny, F. Cuda, S. Maltsev, M. C. Grossel, M. Carravetta and M. H. Levitt, Phys. Rev. Lett. **102**, 013001 (2009).

[4] A. J. Horsewill, S. Rols, M. R. Johnson, Y. Murata, M. Murata, K. Komatsu, M. Carravetta, S. Mamone, M. H. Levitt, J. Y. -C. Chen, J. A. Johnson, X. Lei and N. J. Turro, Phys. Rev. B **82**, 081410(R) (2010).

[5] S. Mamone, J. Y. -C. Chen, R. Bhattacharyya, M. H. Levitt, R. G. Lawler, A. J. Horsewill, T. Rõõm, Z. Bačić and N. J. Turro, Coord. Chem. Rev. **255**, 938 (2011).

[6] L. Ulivi, M. Celli, A. Gianassi, A. J. Ramirez-Cuesta, D. J. Bull and M. Zoppi, Phys. Rev. B **76**, 161401(R) (2007).

[7] K. T. Tait, F. Trouw, Y. Zhao, C. M. Brown and R. T. Downs, J. Chem. Phys. **127**, 134505 (2007).

[8] J. L. C. Rowsell, J. Eckert and O. M. Yaghi, J. Am. Chem. Soc. **127**, 14904 (2005).

[9] F. M. Mulder, T. J. Dingemans, H. G. Schimmel, A. J. Ramirez-Cuesta and G. J. Kearley, Chem. Phys. **351**, 72 (2008).

[10] C. M. Brown, Y. Liu, T. Yildirim, V. K. Peterson and C. J. Kepert, Nanotechnology **20**, 204025 (2009).

[11] P. D. C. Dietzel, P. A. Georgiev, J. Eckert, R. Blom, T. Strässle and T. Unruh, Chem. Commun. **46**, 4962 (2010).

[12] P. A. Georgiev, A. Albinati, B. L. Mojet, J. Ollivier and J. Eckert, J. Am. Chem. Soc. **129**, 8086 (2007).

[13] J. M. Nicol, J. Eckert and J. Howard, J. Phys. Chem. **92**, 7117 (1988).

[14] L. Kong, G. Román-Peréz, J. M. Soler and D. C. Langreth, Phys. Rev. Lett. **103**, 096103 (2009).

[15] M. Xu, Y. Elmatad, F. Sebastianelli, J. W. Moskowitz and Z. Bačić, J. Phys. Chem. B **110**, 24806 (2006).

[16] M. Xu, F. Sebastianelli and Z. Bačić, J. Chem. Phys. **128**, 244715 (2008).

[17] M. Xu, F. Sebastianelli and Z. Bačić, J. Phys. Chem. A **113**, 7601 (2009).

[18] A. Witt, F. Sebastianelli, M. E. Tuckerman and Z. Bačić, J. Phys. Chem. C **114**, 20775 (2010).

[19] M. Xu, F. Sebastianelli, Z. Bačić, R. Lawler and N. J. Turro, J. Chem. Phys. **128**, 011101 (2008).

[20] M. Xu, F. Sebastianelli, B. R. Gibbons, Z. Bačić, R. Lawler and N. J. Turro, J. Chem. Phys. **130**, 224306 (2009).

[21] F. Sebastianelli, M. Xu, Z. Bačić, R. Lawler and N. J. Turro, J. Am. Chem. Soc. **132**, 9826 (2010).

[22] S. Ye, M. Xu, Z. Bačić, R. Lawler and N. J. Turro, J. Phys. Chem. A **114**, 9936 (2010).

[23] A. L. R. Bug and G. J. Martyna, Chem. Phys. **261**, 89 (2000).

[24] J. A. MacKinnon, J. Eckert, D. F. Coker and A. L. R. Bug, J. Chem. Phys. **114**, 10137 (2001).

[25] H. Stein, H. Stiller and R. Stockmeyer, J. Chem. Phys. **57**, 1726 (1972).

[26] D. Colognesi, M. Celli and M. Zoppi, J. Chem. Phys. **120**, 5657 (2004).

[27] J. A. Young and J. U. Koppel, Phys. Rev. **135**, A603 (1964).

[28] M. Zoppi, Physica B **183**, 235 (1993).

[29] M. Xu, L. Ulivi, M. Celli, D. Colognesi and Z. Bačić, Phys. Rev. B **83**, 241403(R) (2011).

[30] S. W. Lovesey. *Theory of neutron scattering from condensed matter, Volume 1.* Oxford University Press, Oxford, (1984).

[31] J. Schwinger and E. Teller, Phys. Rev. **52**, 286 (1937).

[32] V. F. Sears, Canad. J. Phys. **44**, 1279 (1966).

[33] V. F. Sears, Neutron News **3**, (3) 26 (1992).

[34] S. Liu, Z. Bačić, J. W. Moskowitz and K. E. Schmidt, J. Chem. Phys. **103**, 1829 (1995).

[35] Z. Bačić and J. C. Light, Annu. Rev. Phys. Chem. **40**, 469 (1989).

[36] I. Matanović, M. Xu, J. W. Moskowitz, J. Eckert and Z. Bačić, J. Chem. Phys. **131**, 224308 (2009).

[37] J. M. Bowman, T. Carrington and H. D. Meyer, Mol. Phys. **106**, 2145 (2008).

[38] J. V. Lill, G. A. Parker and J. C. Light, J. Chem. Phys. **85**, 900 (1986).

[39] J. C. Light and T. Carrington, Jr., Adv. Chem. Phys **114**, 263 (2000).

[40] D. M. Brink and G. R. Satchler. *Angular momentum.* Clarendon Press, Oxford, (1968).

[41] G. Arfken. *Mathematical Methods for Physicists.* Academic Press, Orlando, FL, (1985).

[42] R. N. Zare. *Angular Momentum: Understanding Spatial Aspects in Chemistry and Physics.* Wiley-Intersience, New York, (1988).