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Experimental confirmation of a predicted selection rule in inelastic neutron scattering spectroscopy: The quantum translator-rotator H_2 entrapped inside C_{60}

Minzhong Xu,¹ Mónica Jiménez-Ruiz,² Mark R. Johnson,² Stéphane Rols,² Shufeng Ye,¹ Marina Carravetta,³ Mark S. Denning,³ Xuegong Lei,⁴ Zlatko Bačić,^{1,5*} and Anthony J. Horsewill^{6†}

¹*Department of Chemistry, New York University, New York, NY 10003, USA*

²*Institut Laue-Langevin, BP 156, 38042 Grenoble, France*

³*School of Chemistry, University of Southampton, Southampton SO17 1BJ, United Kingdom*

⁴*Department of Chemistry, Columbia University, New York, NY 10027, USA*

⁵*NYU-ECNU Center for Computational Chemistry at NYU Shanghai, Shanghai, 200062, China*

⁶*School of Physics & Astronomy, University of Nottingham, Nottingham NG7 2RD, United Kingdom*

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Abstract

We report an inelastic neutron scattering (INS) study of H_2 molecule encapsulated inside the fullerene C_{60} which confirms the recently predicted selection rule, the first to be established for the INS spectroscopy of aperiodic, discrete molecular compounds. Several transitions from the ground state of para- H_2 to certain excited translation-rotation states, forbidden according to the selection rule, are systematically absent from the INS spectra, thus validating the selection rule with a high degree of confidence. Its confirmation sets a precedent, as it runs counter to the widely held view that the INS spectroscopy of molecular compounds is not subject to any selection rules.

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* Electronic mail: zlatko.bacic@nyu.edu

† Electronic mail: a.horsewill@nottingham.ac.uk

The confinement of a light molecule such as H_2 inside a nanosize cavity results in the quantization of the translational motions of the center of mass (c.m.) of H_2 , which couple to the quantized rotational degrees of freedom of the molecule. Inelastic neutron scattering (INS) spectroscopy is a powerful probe for investigating the highly quantum coupled translation-rotation (TR) dynamics of hydrogen molecules entrapped in the nanocavities of diverse host materials [1, 2]. In particular, in recent years it has been used to probe in detail the TR dynamics of a hydrogen molecule encapsulated in the fullerene C_{60} [3–5] and the azacyclic-thiacyclic open-cage fullerene (ATOCF) [6], as well as in the cages of clathrate hydrates [7, 8]. INS was also used to investigate the quantum rotation of H_2O inside C_{60} [9]. The remarkable power of INS stems from two distinctive features. One of them is the unusually large cross section for the incoherent neutron scattering from the hydrogen (^1H) nucleus [10], ~ 15 times greater than for any other nucleus, including deuterium (^2H) [2], which makes INS a highly selective probe of the quantum dynamics of the entrapped hydrogen molecules. The other unique feature of INS is that neutrons, unlike photons, can induce nuclear spin transitions. This allows the observation of rotational $\Delta j = 1$ transitions involving the interconversion between the nuclear spin isomers para- H_2 (total nuclear spin $I = 0$, even rotational quantum numbers $j = 0, 2, \dots$) and ortho- H_2 (total nuclear spin $I = 1$, odd $j = 1, 3, \dots$), which are forbidden in the optical, infrared and Raman spectroscopy. The measured INS spectra contain a wealth of information about the quantum TR dynamics of the guest molecule and its anisotropic interactions with the host cage. However, complete and quantitative extraction of this encoded information is possible only with the help of theory capable of rigorously simulating the INS spectra in their full complexity. This essential prerequisite was met with the recent development of the sophisticated quantum methodology for accurate calculations of the INS spectra, i.e., the energies and the intensities of the TR transitions, of a hydrogen molecule confined inside a nanoscale cavity of an arbitrary shape [11, 12]. The treatment rigorously incorporates the TR dynamics of the nanoconfined H_2 , yielding INS spectra with a uniquely high degree of realism. This has allowed reliable interpretation and assignment of the INS spectra measured for H_2 entrapped in C_{60} [13] and in the cages of clathrate hydrates [14].

Selection rules play a central role in spectroscopy in general, determining whether transitions between certain pairs of states of a system are allowed or forbidden [15]. Knowing them is crucial for the correct interpretation and assignment of the experimental spectra.

It has been taken for granted that the INS spectroscopy of discrete (aperiodic) molecular systems, including supramolecular complexes such as $\text{H}_2@C_{60}$, is not subject to any selection rules [1, 2, 16, 17], in contrast to the optical, infrared (IR) and Raman, spectroscopies. The only known selection rules are the phonon symmetry selection rules established for the coherent INS of crystals [18], based on their space-group symmetry. We have challenged this widely held view recently [13], by deriving a new and entirely unexpected selection rule for the incoherent INS spectra of an H_2 molecule confined in a near-spherical nanocavity, such as that of C_{60} (powdered sample), where the orbital angular momentum associated with the c.m. motion of H_2 and the rotational angular momentum of the molecule couple to give the total angular momentum [13]. The selection rule will be stated explicitly below, after the quantum numbers used to assign the TR eigenstates have been introduced. According to the new selection rule, certain INS transitions involving the ground TR state of p- H_2 are forbidden [13]. Rigorous numerical calculations of the INS spectra of $\text{H}_2@C_{60}$ showed that all the transitions predicted by the selection rule to be forbidden indeed have zero intensity [13].

Establishing for the first time the existence of an INS selection rule for a class of discrete (supra)molecular compounds sets a conceptual precedent, and opens the door to the possibility of hitherto unsuspected selection rules in the INS of other types of molecular systems. It is therefore essential to provide the experimental validation of the new selection rule. In this Letter, we report new INS spectra for $\text{H}_2@C_{60}$ measured at the highest resolution on a new spectrometer, which place extremely low upper limits on several transitions forbidden by the selection rule, thus confirming its validity with a high degree of confidence.

The elegance and apparent simplicity of $\text{H}_2@C_{60}$ conceal surprisingly intricate quantum dynamics arising from the TR coupling induced by the confining potential with icosahedral (I_h) symmetry, which was elucidated in a series of theoretical studies [19–21]. The translational eigenstates can be assigned with the principal quantum number $n = 0, 1, 2, \dots$, of the 3D isotropic harmonic oscillator (HO) and its orbital angular momentum quantum number $l = n, n - 2, \dots, 1$ or 0 , for odd and even n , respectively. The quantum number $j = 0, 1, 2, \dots$, of the rigid rotor can be used for assigning the rotational energy levels of the caged H_2 . The TR states of $\text{H}_2@C_{60}$ excited both translationally and rotationally exhibit the most prominent feature of the “rattling” dynamics of the endohedral hydrogen - strong vectorial coupling of the orbital angular momentum \mathbf{l} and the rotational angular momentum

\mathbf{j} to give the total angular momentum $\boldsymbol{\lambda}$ having the values $\lambda = l + j, l + j - 1, \dots, |l - j|$, with the degeneracy of $2\lambda + 1$ [19]. Due to the TR coupling, the eigenstates with the same quantum numbers n and j (both nonzero) are split into distinct closely spaced energy levels, each labeled with one of the possible values of the quantum number λ , and exhibit the degeneracy of $2\lambda + 1$ [19]. The predicted splitting of the (nine) $n = l = 1, j = 1$ TR eigenstates into three levels corresponding to $\lambda = 1, 2$, and 0 , respectively [19, 21], was subsequently observed in both the IR [22] and INS spectra [4] of $\text{H}_2@C_{60}$.

The INS selection rule introduced by us in Ref. 23 and rigorously proved in Ref. 13 can now be stated as follows: in a near-spherical nanocavity such as that of C_{60} , INS transitions involving the ground TR state $(0, 0, 0, 0)$ of p- H_2 and the excited state (n, j, λ, l) are *forbidden* for $\lambda = j + l - 1$.

It is worth reiterating that the above selection rule is expected to apply only to those systems where the TR coupling is such that it gives rise to the total angular momentum quantum number λ as a good quantum number, as it does in $\text{H}_2@C_{60}$.

The TR motions of H_2 molecule inside a rigid nanocavity can be described in terms of the Cartesian coordinates x, y , and z of the c.m. of H_2 , and the two polar angles θ and ϕ specify the molecule's orientation relative to the cage. Since the three rotational constants of C_{60} are extremely small, 0.347×10^{-3} meV, the fullerene can be treated as nonrotating. This greatly simplifies the 5D TR Hamiltonian of the caged diatomic molecule to [12]

$$H = -\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + B\mathbf{j}^2 + V(x, y, z, \theta, \phi). \quad (1)$$

In Eq. (1), μ is the reduced mass of H_2 in C_{60} , and \mathbf{j}^2 is the angular momentum operator of the diatomic molecule. B denotes the rotational constant of the endohedral H_2 , and $V(x, y, z, \theta, \phi)$ is the 5D intermolecular potential energy surface (PES) for the interaction between the entrapped H_2 and the interior of C_{60} . Accurate TR energy levels and wave functions of $\text{H}_2@C_{60}$, well converged up to about 200 meV, were calculated for the Hamiltonian in Eq. (1), utilizing the efficient computational methodology developed in our group [12] and the 5D PES described previously [13]. The computed lower-lying TR energy levels are shown in Fig. 1. All levels with nonzero n, j quantum numbers are split by the TR coupling into sublevels, each associated with one value of λ , which is a good quantum number. The energy range in Fig. 1 encompasses four transitions out of the ground TR state $(0, 0, 0, 0)$ of p- H_2 which are forbidden by the selection rule, and therefore should not be present in the

measured INS spectra of $\text{H}_2@C_{60}$; the excited states having the forbidden transitions are indicated with the red solid lines.

The sample used in the INS experiments is the same as that reported in Ref. 4 but an additional purification step was performed as follows: (i) the sample was washed with diethyl ether; (ii) to remove occluded solvent the sample was heated to 250°C for 4 h at a pressure of 2×10^{-5} mbar; (iii) the sample was sublimed onto the walls of a silica tube (6 mm outer-diameter). The sublimation was carried out by heating the sample from room temperature to 550°C at 1°C min^{-1} and then maintaining this temperature for 12 h.

The INS spectrum of $\text{H}_2@C_{60}$ presented in Fig. 2 was recorded using the new IN1-Lagrange spectrometer installed at the hot source at the Institut Laue-Langevin in Grenoble. This spectrometer combines an extended energy range, a high resolution, and high flux. Measurements were performed using a Cu(220) monochromator and the energy resolution was $\sim 2\%$ of the energy transfer. Compared with the previous studies [4], this new spectrum substantially extends the range of energy transfer recorded from 60 meV to beyond 250 meV. At the sample temperature of 2.5 K, only the ground TR states $(0, 0, 0, 0)$ of p- H_2 and $(0, 1, 1, 0)$ of o- H_2 are populated. Also, the ortho-para conversion is extremely slow, such that none was observed on the timescale of the experiments (several days). Therefore, the two nuclear spin isomers exist as distinct species and all INS transitions must originate in their respective ground states, either $(0, 0, 0, 0)$ or $(0, 1, 1, 0)$. Superimposed on the measured INS spectrum in Fig. 2(a) is the stick spectrum of $\text{H}_2@C_{60}$ calculated with our recently developed quantum methodology for accurate simulation of the INS spectra [11, 12], which utilizes the 5D TR wave functions of the Hamiltonian in Eq. (1). The statistical 3:1 mixture of o- H_2 and p- H_2 expected for the high temperature at which $\text{H}_2@C_{60}$ is prepared [24] was assumed in the simulations. In Fig. 2(b), the comparison is made to the stick spectrum convoluted with the resolution function appropriate for the spectrometer. It is evident from even a cursory inspection of both panels that the measured and calculated INS spectra are in a remarkable agreement over the entire energy range shown. This means that the rich information content of the new INS measurements can be analyzed in full and quantitatively, which will be reported in a separate publication.

We now focus on the transitions which the selection rule predicts to be forbidden. The first such transition, $(0, 0, 0, 0) \rightarrow (1, 1, 1, 1)$, belongs to the triplet of transitions $(0, 0, 0, 0) \rightarrow (1, 1, \lambda, 1)$ $\lambda = 1, 2, 0$, in the region centered at 37.5 meV where a doublet is observed,

shown in the top panel of Fig. 3. Based on the measured (allowed) transition $(0, 1, 1, 0) \rightarrow (1, 1, 1, 1)$, this forbidden transition should occur at 36.87 meV. According to the calculations [13], the $\lambda = 2$ and $\lambda = 0$ components have successively higher energies. Therefore, the peak at 37.41 meV is assigned to the $\lambda = 2$ component of the triplet and the 38.55 meV peak to the $\lambda = 0$ component. Additional support for this assignment comes from the fact that the calculated intensity ratio of the $\lambda = 2$ and $\lambda = 0$ transitions, 2.08:1, matches almost perfectly the measured intensity ratio of 2.14:1. There is no evidence at all of the $\lambda = 1$ component of the triplet, consistent with it being forbidden by the selection rule. Fitting this spectrum with three Gaussians enabled us to place an upper limit on the intensity of the forbidden peak at 36.87 meV to no more than 1% of the intensity of the $(0, 0, 0, 0) \rightarrow (1, 1, 2, 1)$ transition.

Two other forbidden transitions originating in the ground TR state of p-H₂ are $(0, 0, 0, 0) \rightarrow (2, 1, 2, 2)$ and $(0, 0, 0, 0) \rightarrow (3, 1, 3, 3)$. In both these cases the energies of the final states are known from the peaks in the spectrum that originate from the ground TR state $(0, 1, 1, 0)$ of o-H₂. As shown in the middle panel of Fig. 3, the $\lambda = 3, 1$ components of the $(0, 0, 0, 0) \rightarrow (2, 1, \lambda, 2)$ multiplet closely overlap as a single line centered on 61.29 meV. The $(0, 0, 0, 0) \rightarrow (2, 1, 2, 2)$ component, forbidden according to the selection rule, should occur at 60.19 meV, but is absent from the spectrum. Attempting a fit in this region led us to conclude that the intensity of this forbidden peak is at most 1% of the 61.29 meV peak.

Similarly, the bottom panel of Fig. 3 shows that the $(3, 1, 4, 3)$ and $(3, 1, 2, 3)$ components of the multiplet $(0, 0, 0, 0) \rightarrow (3, 1, \lambda, 3)$ closely overlap, along with $(0, 0, 0, 0) \rightarrow (0, 3, 3, 0)$, in forming the peak centered on 86.52 meV. The peak associated with the forbidden $\lambda = 3$ component would appear 1.1 meV lower in energy, but is absent from the spectrum. Fitting this region of the spectrum we concluded that the intensity of the forbidden $(0, 0, 0, 0) \rightarrow (3, 1, 3, 3)$ peak is less than 1% of the 86.52 meV peak.

The forbidden transition $(0, 0, 0, 0) \rightarrow (1, 2, 2, 1)$ according to the quantum calculations [13] almost coincides with the intense transition $(0, 0, 0, 0) \rightarrow (2, 1, 1, 0)$ observed at 64.14 meV, see the middle panel of Fig. 3 and also the TR energy level diagram in Fig. 1. Therefore it is not possible to ascertain the zero intensity of this forbidden transition in the experimental spectrum. At higher energies, forbidden transitions $(0, 0, 0, 0) \rightarrow (3, 1, 1, 1)$ and $(4, 1, 2, 2)$ are predicted by the selection rule. However, with increasing energy there are

many overlapping lines and the resolution is insufficient to confirm that the intensities of the forbidden transitions in the experimental spectrum are zero.

In summary, the measured INS spectra of $\text{H}_2@C_{60}$ presented here confirm with a high degree of confidence the validity of the recently derived selection rule [13], the first ever to be established for the incoherent INS of a class of aperiodic, discrete molecular compounds. In three instances, the transitions which the selection rule predicts to be forbidden are systematically absent from the spectrum, placing very low upper limits on their intensities. Although the present selection rule [13] applies to a special class of endohedral complexes with high symmetry, experimental confirmation of its existence contradicts, and mandates the revision of, the near-universal consensus that the INS of molecular compounds is free from any selection rules. Establishing this precedent should stimulate the search for new selection rules which may be operational in the INS of other types of discrete molecular compounds.

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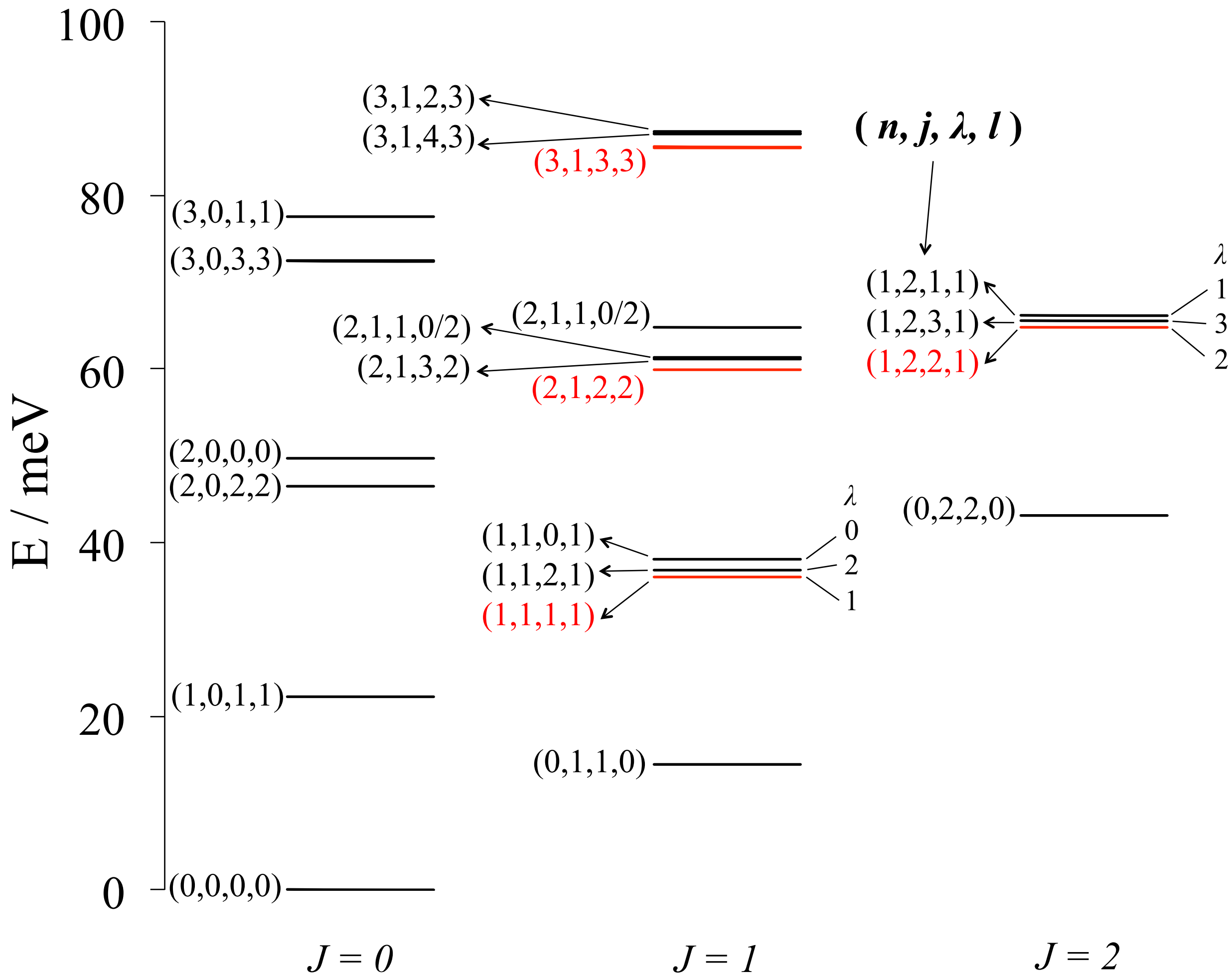
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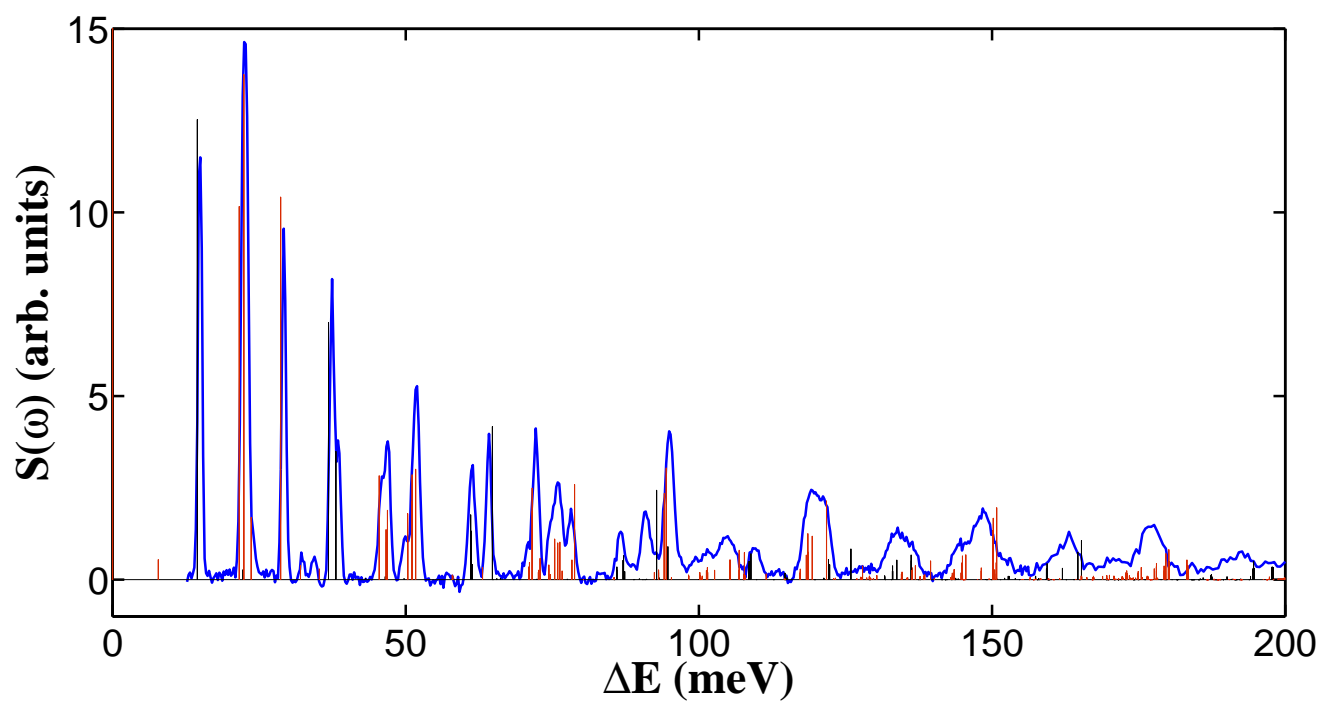
FIG. 1: Lower-lying TR energy levels of p-H₂ and o-H₂ molecules inside C₆₀ from the quantum 5D calculations. They are labeled by the quantum numbers (n, j, λ, l) defined in the text, and are arranged in columns according to their j values. The four transitions from the ground TR state $(0, 0, 0, 0)$ of p-H₂ to those marked with red lines are forbidden according to the selection rule.

FIG. 2: The INS spectrum of H₂@C₆₀ recorded on the IN1-Lagrange spectrometer, at 2.5K. Superimposed on it for comparison are (a) the calculated stick spectrum, and (b) the stick spectrum convolved with the experimental resolution function.

FIG. 3: Expanded view of the measured INS spectrum in the energy regions containing the forbidden transitions. Dashed lines represent Gaussian fits to the individual components of the bands, and solid lines the overall fit to the experimental data. Dashed arrows mark the expected positions of the forbidden transitions.



a)



b)

