Nonrigid Group Theory, Tunneling Splittings, and Nuclear Spin Statistics of Water Pentamer: $(H_2O)_5$

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The character table of the fully nonrigid water pentamer, $(H_2O)_5$, is derived for the first time. The group of all feasible permutations is the wreath product group $S_5[S_2]$ and it consists of 3840 operations divided into 36 conjugacy classes and irreducible representations. We have shown that the full character table can be constructed using elegant matrix type generator algebra. The character table has been applied to the water pentamer by obtaining the nuclear spin statistical weights of the rovibronic levels and tunneling splittings of the fully nonrigid pentamer. We have also obtained the statistical weights and tunneling splittings of a semirigid deuterated pentamer that exhibits pseudorotation with an averaged C_{5h} (G_{10}) symmetry used in the assignment of vibration-rotation−tunneling spectra. It is also shown that the previously considered group G_{320} for water pentamer of feasible permutations is a subgroup of the full group and is the direct product of wreath product $C_5[S_2]$ and the inversion group. The correlation tables have been constructed for the semirigid (G_{10}) to nonrigid (G_{3840}) groups for the rotational levels and tunneling levels. The nuclear spin statistical weights have also been derived for both the limits and through the use of subduced representations the corresponding information can be obtained for G(320) as well from G(3840).

1. Introduction

Laser spectroscopy and dynamics of water clusters have been the topic of numerous studies for many years.[1−12] Water clusters are particularly intriguing owing to the interplay of hydrogen bonding and floppy motions that result in novel quantum tunneling dynamics.[1−15] Some of the water clusters also exhibit chirality in their equilibrium geometries and thus quantum tunneling among chiral isomers has received attention.[2,3,11] One of the reasons for so much activity and interest in studying water clusters is that such studies could provide significant insight into aqueous process in chemistry and biology.[2] Many of these studies have been motivated by compelling need to understand liquid water, and how molecular clusters evolve into liquid state.

The pentamer of water, $(H_2O)_5$, has received considerable attention[2,6−9] owing to its interesting dynamics, chirality, and the fact that the pentagonal rings of water molecules occur in nature as calthrate hydrates and solvation of hydrophobic groups in biosystems. Furthermore, a five-membered cluster of water seems to have a dominant population and role in liquid water simulations. For these reasons, $(H_2O)_5$ has been the focus of several spectroscopic studies.[6−9] Liu et al.[8] have employed terahertz laser spectroscopy for detailed analysis of vibration−rotation-tunneling spectra of $(D_2O)_5$. The spectra revealed that, although the pentamer exhibits a chiral asymmetric five-member ring geometry as its equilibrium structure (shown in Figure 1), the observed spectra of $(D_2O)_5$ are consistent with a pseudorotation model that yields averaged rotational constants that correspond to an achiral quasi-planar C_{5h} oblate top geometry. The authors[8] have also noted that facile flipping motions of protons are feasible owing to low barriers and that should yield a nonrigid pentamer, especially for the protonated form. In a more recent study Keutsch and Saykally[2] have shown that for the pentamer, which has a chiral equilibrium structure, allows for very facile torsional tunneling motions and thus bifurcation tunneling splitting which connects 32 degenerate minima have been observed in $(H_2O)_5$ although somewhat reduced compared to $(H_2O)_3$. The most recent study on water clusters by Goldman and Saykally[1] deals with diffusion Monte Carlo methods for ground vibrational properties of water clusters.

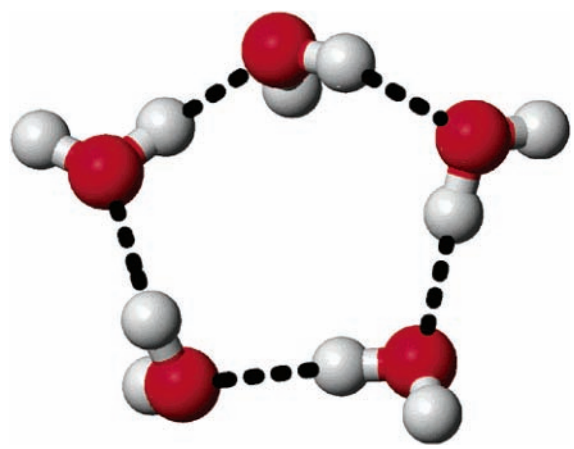

Figure 1. Equilibrium Geometry of $(H_2O)_5$ in its cyclic chiral form with no symmetry.

As noted by the above survey, water clusters in general and the water pentamer in particular exhibit nonrigid tunneling motions among several potential minima separated by surmountable energy barriers. Although the extent of tunneling

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would depend on the actual barriers, there is a compelling need to consider the molecular symmetry groups of the nonrigid cluster from semirigid to fully nonrigid limits. Longuet-Higgins[16] has formulated the symmetry groups of nonrigid molecules as permutation−inversion groups by including all feasible permutations of the nuclei under such fluxional or tunneling motions. Up to now, the full character table of the fully nonrigid $(H_2O)_5$ pentamer has not been obtained. The present author has shown that the groups of nonrigid molecules can be expressed as wreath product groups and as generalized wreath products.[15,17−20] These groups have also been used in a number of chemical applications such as enumeration of isomers,[23,24] weakly bound van der Waals, or hydrogen-bonded complexes such as $(NH_3)_2$, $(H_2O)_2$, $(C_6H_6)_2$, etc.,[12−15,21] polyhedral structures,[25,26] spectroscopy,[13,14,21,22] and clusters.[27] King[25,26] has applied the wreath product groups to represent the symmetries of four-dimensional analogues of polyhedra. Thus, apart from the current motivation of $(H_2O)_5$, there is considerable interest in the wreath product groups of higher order and their character tables. The present author[15] has applied combinatorial methods without the construction of the character tables for the spin statistics of protonated forms of water clusters. However, the character tables, tunneling splittings, and correlation of the rotational and rovibronic levels from semirigid to fully nonrigid limits have not been considered as character tables of the larger groups such as the one for fully nonrigid $(H_2O)_5$ have not been derived. Wales and coworkers[31−33] have considered both BLYP computations with double-ζ basis and permutation-inversion groups of water trimer to pentamer. In particular for the $(H_2O)_5$ pentamer cluster, Wales and Walsh[32] have considered the permutation-inversion group on the basis of computed energetics of the various rearrangement pathways. The group that they have obtained by allowing the single flip and bifurcation tunneling mechanisms for the cyclic global minimum is a group of order 320 denoted by them as G_{320}. In this investigation, we show that this group is a subgroup of the wreath product $S_5[S_2]$ X I that we have considered here, and in fact it is the direct product C_5 $[S_2]$ X I, where only the permutations in the cyclic group C_5 are included. We also show that all of the results that we have obtained can be reduced to the G_{320} group by the use of subduced representations.

In this study, we have considered the development of the character table of the nonrigid $(H_2O)_5$ in its full nonrigid limit. By this it is meant that all possible “flippings” or permutations of the protons on each water molecule are considered. Since the barriers for such motions are surmountable depending on the experimental conditions, the full group would comprise of all feasible permutations of protons arising from the flipping motion on each water molecule and the permutations of the water molecules. The resulting group is shown to be the wreath product $S_5[S_2]$, where the group S_n is a permutation group of n! operations, and the square bracket symbol stands for wreath products. We show that the fully nonrigid $(H_2O)_5$ exhibits a group of 3840 operations divided into 36 conjugacy classes and 36 irreducible representations. We have obtained the character table of this group for the first time, and we have applied the character table to correlate the rotational levels and nuclear spin statistical weights from a semirigid $(H_2O)_5$ to a fully nonrigid $(H_2O)_5$. The nuclear spin statistical weights show that only some of the tunneling levels are significantly populated.

2. Wreath Product Group $S_5[S_2]$ for $(H_2O)_5$

Although the theory of wreath product groups and the related mathematical details have been described in sufficient details elsewhere,[17,18] we provide here the salient points so that the work is sufficiently self-contained for $(H_2O)_5$. All our illustrations will thus be restricted only to $(H_2O)_5$. Suppose G is a group of permutations of some nuclei and H be another permutation group of nuclei. For the case of $(H_2O)_5$, the group G consists of the permutations of the oxygen nuclei in the fully nonrigid limit where they are allowed to exchange and H is the permutations of the protons owing to the facile flipping motion. Thus, the group G is the set of 5! permutations of five O nuclei, and H is the group S_2 of protons on each water molecule that correspond to the flipping motion which exchanges these protons. In general, the permutation S_n group[28−30] consists of n! permutations of n objects of a set of chosen nuclei, denoted by Ω to represent the rigid framework. Note that the notation S_n that we use here differs from the point group S_n that corresponds to an n-fold improper axis of rotation. All references to S_n in this work would mean the permutation group of n! operations. As the oxygen atoms get permuted, they also carry with them the protons attached to them, and thus, they induce permutations of the protons also. Consequently, the overall group of $(H_2O)_5$ becomes the wreath product of G with H, denoted by G[H], which becomes $S_5[S_2]$ in this case. The wreath product group G[H] is defined as the set of permutations

$$\{(g;\pi)|\ \pi \text{ mapping of } \Omega \text{ into H, } g\epsilon G\}$$

such that the product of two permutations is defined as

$$(g;\pi)(g;\pi') = (gg';\pi\pi_g{}')$$

where

$$\pi_g(i) = \pi(g^{-1}i),\ \forall\ i\epsilon\Omega$$

$$\pi\pi'(i) = \pi(i)\pi'(i),\ \forall\ i\epsilon\Omega$$

An element of G[H] is represented by (g; h_1, h_2,.....h_n), where gϵG and $h_i\epsilon$H. Thus, the group G[H] contains $|G||H|^n$ elements where n is the order of Ω. In the case of $(H_2O)_5$, the full nonrigid permutation group’s order is given by

$$|S_5[S_2]| = 5!\ (2!)^5 = 3840$$

The group $S_5[S_2]$ is isomorphic with

$$S_5[S_2] = (S_2 \times S_2 \times S_2 \times S_2 \times S_2) \wedge S_5{}'$$

where five copies of the same group S_2 are multiplied, $\times$ symbol stands for direct product, whereas ^ symbol represents a semidirect product.

The conjugacy classes of the wreath product $S_5[S_2]$ group are obtained as matrix types from the permutation cycle type or orbit structure of g in S_5 and the conjugacy class information of S_2. Let a permutation gϵS_5 generate a_1 cycles of length 1, a_2 cycles of length 2,.....a_5 cycles of length 5 upon its action on the set Ω. The cycle type of g is then denoted by $T_g = (a_1, a_2, ..., a_5)$. To illustrate a permutation (12)(345) of the oxygen nuclei would have the cycle type (0,1,1,0,0) as it generates one cycle of length 2 and one cycle of length 3. Since there are only two conjugacy classes for S_2, we may denote them by C_1 and C_2. The cycle type of an element in the wreath product $S_5[S_2]$ can be expressed by a 2 $\times$ 5 matrix, T(g;π) also known as the cycle type of (g;π). It is obtained by investigating the orbit structure of g and the conjugacy class of S_2. That is, suppose a_{ik} of the cycle products of g belong to the conjugacy class C_i, we obtain

TABLE 1: Conjugacy Classes of the $S_5[S_2]$ Group

no	matrix type	permutation	number of elements	no	matrix type	permutation	number of elements
1	$\begin{bmatrix}5&0&0&0&0\\0&0&0&0&0\end{bmatrix}$	1^{10}	1	2	$\begin{bmatrix}4&0&0&0&0\\1&0&0&0&0\end{bmatrix}$	$1^{8}2$	5
3	$\begin{bmatrix}3&0&0&0&0\\2&0&0&0&0\end{bmatrix}$	$1^{6}2^{2}$	10	4	$\begin{bmatrix}2&0&0&0&0\\3&0&0&0&0\end{bmatrix}$	$1^{4}2^{3}$	10
5	$\begin{bmatrix}1&0&0&0&0\\4&0&0&0&0\end{bmatrix}$	$1^{2}2^{4}$	5	6	$\begin{bmatrix}0&0&0&0&0\\5&0&0&0&0\end{bmatrix}$	2^{5}	1
7	$\begin{bmatrix}3&1&0&0&0\\0&0&0&0&0\end{bmatrix}$	$1^{6}2^{2}$	20	8	$\begin{bmatrix}3&0&0&0&0\\0&1&0&0&0\end{bmatrix}$	$1^{6}4$	20
9	$\begin{bmatrix}2&1&0&0&0\\1&0&0&0&0\end{bmatrix}$	$1^{4}2^{3}$	60	10	$\begin{bmatrix}2&0&0&0&0\\1&1&0&0&0\end{bmatrix}$	$1^{4}24$	60
11	$\begin{bmatrix}1&1&0&0&0\\2&0&0&0&0\end{bmatrix}$	$1^{2}2^{4}$	60	12	$\begin{bmatrix}1&0&0&0&0\\2&1&0&0&0\end{bmatrix}$	$1^{2}2^{2}4$	60
13	$\begin{bmatrix}0&1&0&0&0\\3&0&0&0&0\end{bmatrix}$	2^{5}	20	14	$\begin{bmatrix}0&0&0&0&0\\3&1&0&0&0\end{bmatrix}$	$2^{3}4$	20
15	$\begin{bmatrix}2&0&1&0&0\\0&0&0&0&0\end{bmatrix}$	$1^{4}3^{2}$	80	16	$\begin{bmatrix}2&0&0&0&0\\0&0&1&0&0\end{bmatrix}$	$1^{4}6$	80
17	$\begin{bmatrix}1&0&1&0&0\\1&0&0&0&0\end{bmatrix}$	$1^{2}23^{2}$	160	18	$\begin{bmatrix}1&0&0&0&0\\1&0&1&0&0\end{bmatrix}$	$1^{2}26$	160
19	$\begin{bmatrix}0&0&1&0&0\\2&0&0&0&0\end{bmatrix}$	$3^{2}2^{2}$	80	20	$\begin{bmatrix}0&0&0&0&0\\2&0&1&0&0\end{bmatrix}$	$2^{2}6$	80
21	$\begin{bmatrix}1&2&0&0&0\\0&0&0&0&0\end{bmatrix}$	$1^{2}2^{4}$	60	22	$\begin{bmatrix}0&2&0&0&0\\1&0&0&0&0\end{bmatrix}$	2^{5}	60
23	$\begin{bmatrix}1&1&0&0&0\\0&1&0&0&0\end{bmatrix}$	$1^{2}2^{2}4$	120	24	$\begin{bmatrix}0&1&0&0&0\\1&1&0&0&0\end{bmatrix}$	$2^{3}4$	120
25	$\begin{bmatrix}1&0&0&0&0\\0&2&0&0&0\end{bmatrix}$	$1^{2}4^{2}$	60	26	$\begin{bmatrix}0&0&0&0&0\\1&2&0&0&0\end{bmatrix}$	24^{2}	60
27	$\begin{bmatrix}1&0&0&1&0\\0&0&0&0&0\end{bmatrix}$	$1^{2}4^{2}$	240	28	$\begin{bmatrix}1&0&0&0&0\\0&0&0&1&0\end{bmatrix}$	$1^{2}8$	240
29	$\begin{bmatrix}0&0&0&1&0\\1&0&0&0&0\end{bmatrix}$	24^{2}	240	30	$\begin{bmatrix}0&0&0&0&0\\1&0&0&1&0\end{bmatrix}$	2 8	240
31	$\begin{bmatrix}0&1&1&0&0\\0&0&0&0&0\end{bmatrix}$	$2^{2}3^{2}$	160	32	$\begin{bmatrix}0&1&0&0&0\\0&0&1&0&0\end{bmatrix}$	$2^{2}6$	160
33	$\begin{bmatrix}0&0&1&0&0\\0&1&0&0&0\end{bmatrix}$	$4\ 3^{2}$	160	34	$\begin{bmatrix}0&0&0&0&0\\0&1&1&0&0\end{bmatrix}$	4 6	160
35	$\begin{bmatrix}0&0&0&0&1\\0&0&0&0&0\end{bmatrix}$	5^{2}	384	36	$\begin{bmatrix}0&0&0&0&0\\0&0&0&0&1\end{bmatrix}$	10	384

the cycle type of $(g;\pi)$, which represents the conjugacy class of $S_5[S_2]$ as

$$T(g;\pi) = a_{ik}\ (1 \leq i \geq 2,\ 1 \leq k \geq 5)$$

Table 1 shows all of the cycle matrix types for the conjugacy classes of the nongroup of $(H_2O)_5$, viz., the $S_5[S_2]$ group. Let P(m) denote the number of partitions of integer m with the convention that P(0) = 1. Let 5 be partitioned into ordered pairs as there are only 2 conjugacy classes in the S_2 group, denoted by $(n) = (n_1,n_2)$ such that $\sum_i n_i = n$. Hence the number of conjugacy classes of $S_5[S_2]$ is given by

$$\sum_n P(n_1)P(n_2)$$

The ordered partitions of 5 into 2 parts are (5,0), (0,5), (4,1), (1,4), (3,2), and (2,3) since the S_2 group has 2 conjugacy classes. Substituting the values of P(5) = 7, P(4) = 5, P(3) = 2, P(2) = 2, and P(0) = 1 in the above expression, we obtain the number of conjugacy classes of $S_5[S_2]$ as $2 \times 7 + 2 \times 4 + 2 \times 3 \times 2 = 36$. All 36 conjugacy classes of the $S_5[S_2]$ group are shown in Table 1. The number of elements in each conjugacy class of $S_n[S_2]$ is given by

$$\frac{n!2^n}{\prod_{i,k} a_{ik}!(2k)^{a_{ik}}}$$

To illustrate consider the number of elements in the tenth conjugacy class with the matrix type

$$\begin{bmatrix}2&0&0&0&0\\1&1&0&0&0\end{bmatrix}$$

is given by

$$\frac{5!(2!)^5}{2!(2.1)^2 1!(2.1)^1 1!(2.2)^1} = 60$$

Thus, $5!2^5 = 3840$ operations are divided into 36 conjugacy classes with number of elements in each class obtained using the above formula. All conjugacy classes together with their cycle types and the number of elements in each class are shown in Table 1.

Next we obtain the character table of the $S_5[S_2]$ group with a combinatorial matrix generating function that uses matrix type polynomials. All possible irreducible representations of the $S_5[S_2]$ group can be derived using induced representations from a smaller group to a larger group. The irreducible representations of the S_n group[28,30] are represented by the partitions of n, denoted by $[n_1\ n_2...n_m]$, where n_1, $n_2...n_m$ is a partition of n. Thus, the irreducible representations of the S_5 group are given by [5], [41], [32], $[31^2]$, $[2^2\ 1]$, $[21^3]$, and $[1^5]$, whereas the S_2 group has only [2] and $[1^2]$ representations. The irreducible representations of $S_5[S_2]$ are constructed by first forming the outer tensor (outer direct) products of the irreducible representations of S_2 five times, then finding the inertia factor of each such product, and subsequently inducing the representation from the inertia factor group to the whole group. First the unique outer products for the irreducible representations of $S_2 \times S_2 \times S_2 \times S_2 \times S_2$ are constructed as

$$[2]\#[2]\#[2]\#[2]\#[2],\ [2]\#[2]\#[2]\#[2]\#[1^2],\ [2]\#[2]\#[2]\#[1^2]\#[1^2],\ [2]\#[2]\#[1^2]\#[1^2].\ [1^2] \text{ and } [2]\#[1^2]\#[1^2]\#[1^2]\#[1^2] \text{ and } [1^2]\#[1^2]\#[1^2]\ [1^2]\#[1^2]$$

The inertia factor groups (subgroup of S_5) of the above six products are S_5', S_4x S_1' (identity group), S_3x S_2', S_2x S_3', S_1x S_4' and S_5' respectively. All representations of the $S_5[S_2]$ groups are obtained by multiplying the unique outer products of irreducible representations as obtained above with the irreducible representations of the factor group G′ for each product and then inducing the whole representation into $S_5[S_2]$. The irreducible representations are given by

$$F^* = (F_1\#F_2\#......F_5) \otimes F' \uparrow S_5[S_2]$$

where $F_1\#\ F_2\#....F_5$ is the outer tensor product of the irreducible representations (F_1, F_2, ..., F_5) from the group S_2, # is the outer product, F′ is an irreducible representation of the factor group G′, ⊗ represents an inner product, and the ↑ stands for an induced representation to the whole group G[H]. Table 2 shows all 36 irreducible representations thus enumerated for the $S_5[S_2]$ group together with labels for the irreducible representations according to the dimensions of the representations.

The character table of the $S_5[S_2]$ group is generated using the generating functions as polynomials of matrix cycle types. The present author[18] has developed a general algorithm for the characters of the wreath product groups. Let P_G^{χ} be the generalized character cycle index polynomial of the irreducible representation χ of the factor subgroup G′ of G, given by

$$P_G^{\chi} = \frac{1}{|G|}\sum_{g\epsilon G}\chi(g)s_1^{b_1}\ s_2^{b_2}......s_n^{bn}$$

Let $T(M)_i$ be the matrix type of the representation of the inertia factor. The generating function for the irreducible representation F^* of $S_n[S_2]$ is obtained by the replacement

$$T(G[H])^{F^*} = P_G^{\chi}(s_i \rightarrow T(M)_i)$$

In the above expression, every s_i is replaced by the correpsonding matrix type $T(M)_i$, where all algebraic manuiputalions are done with the cycle type matrices. We have introduced ⊕, ⊗, and − opertaions for additions, multiplications, and subtractions to contrast that these are not ordinary matrix multiplications, etc.

TABLE 2: Irreducible Representations of the $S_5[S_2]$ Group

label	irreducible representation	dimension
A_1	$([2]\#[2]\#[2]\#[2]\ \#[2]) \otimes [5]'$	1
G_1	$([2]\#[2]\#[2]\#[2]\ \#[2]) \otimes [41]'$	4
H_1	$([2]\#[2]\#[2]\#[2]\#[2]) \otimes [32]'$	5
I_1	$([2]\#[2]\#[2]\#[2]\#[2]) \otimes [31^2]'$	6
H_2	$([2]\#[2]\#[2]\#[2]\#[2]) \otimes [2^21]'$	5
G_2	$([2]\#[2]\#[2]\#[2]\ \#[2]) \otimes [21^3]'$	4
A_2	$([2]\#[2]\#[2]\#[2]\ \#[2]) \otimes [1^5]'$	1
G_1	$([2]\#[2]\#[2]) \otimes [3]'\ \#([1^2] \otimes [1]'$	4
A_3	$([1^2]\#[1^2]\#[1^2]\#[1^2]\ \#[1^2]) \otimes [5]'$	1
G_3	$([1^2]\#[1^2]\#[1^2]\#[1^2]\ \#[1^2]) \otimes [41]'$	4
H_3	$([1^2]\#[1^2]\#[1^2]\#[1^2]\ \#[1^2]) \otimes [32]'$	5
I_2	$([1^2]\#[1^2]\#[1^2]\#[1^2]\ \#[1^2]) \otimes [31^2]'$	6
H_4	$([1^2]\#[1^2]\#[1^2]\#[1^2]\ \#[1^2]) \otimes [2^21]'$	5
G_4	$([1^2]\#[1^2]\#[1^2]\#[1^2]\ \#[1^2]) \otimes [21^3]'$	4
A_4	$([1^2]\#[1^2]\#[1^2]\#[1^2]\ \#[1^2]) \otimes [1^5]'$	1
H_5	$([2]^4) \otimes [4]'\ \#([1^2] \otimes [1]')$	5
R_1	$([2]^4) \otimes s\ [31]'\ \#([1^2] \otimes [1]')$	15
M_1	$([2]^4) \otimes [2^2]'\ \#([1^2] \otimes [1]')$	10
R_2	$([2]^4) \otimes [21^2]'\ \#([1^2] \otimes [1]')$	15
H_6	$([2]^4) \otimes [1^4]'\ \#([1^2] \otimes [1]')$	5
H_7	$([1^2]^4) \otimes [4]'\ \#([2] \otimes [1]')$	5
R_3	$([1^2]^4) \otimes [31]'\ \#([2] \otimes [1]')$	15
M_2	$([1^2]^4) \otimes [2^2]'\ \#([2] \otimes [1]')$	10
R_4	$([1^2]^4) \otimes [21^2]'\ \#([2] \otimes [1]')$	15
H_8	$([1^2]^4) \otimes [1^4]'\ \#([2] \otimes [1]')$	5
M_3	$([2]^3) \otimes [3]'\ \#([1^2]^2 \otimes [2]')$	10
W_1	$([2]^3) \otimes [21]'\ \#([1^2]^2 \otimes [2]')$	20
M_4	$([2]^3) \otimes [1^3]'\ \#([1^2]^2 \otimes [2]')$	10
M_5	$([2]^3) \otimes [3]'\ \#([1^2]^2 \otimes [1^2]')$	10
W_2	$([2]^3) \otimes [21]'\ \#([1^2]^2 \otimes [1^2]')$	20
M_6	$([2]^3) \otimes [1^3]'\ \#([1^2]^2 \otimes [1^2]')$	10
M_7	$([1^2]^3) \otimes [3]'\ \#([2]^2 \otimes [2]')$	10
W_3	$([1^2]^3) \otimes [21]'\ \#([2]^2 \otimes [2]')$	20
M_8	$([1^2]^3) \otimes [1^3]'\ \#([2]^2 \otimes [2]')$	10
M_9	$([1^2]^3) \otimes [3]'\ \#([2]^2 \otimes [1^2]')$	10
W_4	$([1^2]^3) \otimes [21]'\ \#([2]^2 \otimes [1^2]')$	20
M_{10}	$([1^2]^3) \otimes [1^3]'\ \#([2]^2 \otimes [1^2]')$	10

We shall illustarte this procedure with a few examples. Consider the G_1 irerducible representation given by $([2]^5) \otimes [41]'$. The generalized character cycle index of [41]′, the factor group irreducibe representation, is given by

$$P_{S_5}^{[41]} = \frac{1}{120}[4{s_1}^5 + 20{s_1}^3s_2 + 20{s_1}^2s_3 - 20s_2s_3 - 24s_5]$$

For the representation [2], the matrix type expressions $T(M)_i$ are given as follows:

$$T(M)_1{}^{[2]} = \frac{1}{2}\left[\begin{bmatrix}1&0&0&0&0\\0&0&0&0&0\end{bmatrix} \oplus \begin{bmatrix}0&0&0&0&0\\1&0&0&0&0\end{bmatrix}\right]$$

$$T(M)_2{}^{[2]} = \frac{1}{2}\left[\begin{bmatrix}0&1&0&0&0\\0&0&0&0&0\end{bmatrix} \oplus \begin{bmatrix}0&0&0&0&0\\0&1&0&0&0\end{bmatrix}\right]$$

$$T(M)_3{}^{[2]} = \frac{1}{2}\left[\begin{bmatrix}0&0&1&0&0\\0&0&0&0&0\end{bmatrix} \oplus \begin{bmatrix}0&0&0&0&0\\0&0&1&0&0\end{bmatrix}\right]$$

$$T(M)_4{}^{[2]} = \frac{1}{2}\left[\begin{bmatrix}0&0&0&1&0\\0&0&0&0&0\end{bmatrix} \oplus \begin{bmatrix}0&0&0&0&0\\0&0&0&1&0\end{bmatrix}\right]$$

$$T(M)_5{}^{[2]} = \frac{1}{2}\left[\begin{bmatrix}0&0&0&0&1\\0&0&0&0&0\end{bmatrix} \oplus \begin{bmatrix}0&0&0&0&0\\0&0&0&0&1\end{bmatrix}\right]$$

Replacing every s_i by $T(M)_i$ in the expression for $P_{S_5}^{[41]}$ we obtain

$$GF_{G_1} = \frac{1}{5!}\left\{4\left\{\frac{1}{2}\left(\begin{bmatrix}1 & 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0 & 0\end{bmatrix} \oplus \begin{bmatrix}0 & 0 & 0 & 0 & 0\\ 1 & 0 & 0 & 0 & 0\end{bmatrix}\right)\right\}^5 + 20 \left\{\frac{1}{2}\left(\begin{bmatrix}1 & 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0 & 0\end{bmatrix} \oplus \begin{bmatrix}0 & 0 & 0 & 0 & 0\\ 1 & 0 & 0 & 0 & 0\end{bmatrix}\right)\right\}^3 \frac{1}{2}\left(\begin{bmatrix}0 & 1 & 0 & 0 & 0\\ 0 & 0 & 0 & 0 & 0\end{bmatrix} \oplus \begin{bmatrix}0 & 0 & 0 & 0 & 0\\ 0 & 1 & 0 & 0 & 0\end{bmatrix}\right) - 20\frac{1}{2}\left(\begin{bmatrix}0 & 1 & 0 & 0 & 0\\ 0 & 0 & 0 & 0 & 0\end{bmatrix} \oplus \begin{bmatrix}0 & 0 & 0 & 0 & 0\\ 0 & 1 & 0 & 0 & 0\end{bmatrix}\right) \times \frac{1}{2}\left(\begin{bmatrix}0 & 0 & 1 & 0 & 0\\ 0 & 0 & 0 & 0 & 0\end{bmatrix} \oplus \begin{bmatrix}0 & 0 & 0 & 0 & 0\\ 0 & 0 & 1 & 0 & 0\end{bmatrix}\right) - 24\frac{1}{2}\left(\begin{bmatrix}0 & 0 & 0 & 0 & 1\\ 0 & 0 & 0 & 0 & 0\end{bmatrix} \oplus \begin{bmatrix}0 & 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0 & 1\end{bmatrix}\right)\right\}$$

By use of the matrix manipulations for the cycle types where the multiplication of two matrix cycle types is interpreted as ordinary matrix additions, we can simplify the above expression as

$$\begin{aligned} GF_{G_1} = \frac{1}{5!}\frac{1}{2^5}\Big\{ & 4\begin{bmatrix}5 & 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0 & 0\end{bmatrix} + 20\begin{bmatrix}4 & 0 & 0 & 0 & 0\\ 1 & 0 & 0 & 0 & 0\end{bmatrix} + 40\begin{bmatrix}3 & 0 & 0 & 0 & 0\\ 2 & 0 & 0 & 0 & 0\end{bmatrix} + 40\begin{bmatrix}2 & 0 & 0 & 0 & 0\\ 3 & 0 & 0 & 0 & 0\end{bmatrix} + \\ & 20\begin{bmatrix}1 & 0 & 0 & 0 & 0\\ 4 & 0 & 0 & 0 & 0\end{bmatrix} + 4\begin{bmatrix}0 & 0 & 0 & 0 & 0\\ 5 & 0 & 0 & 0 & 0\end{bmatrix} + 40\begin{bmatrix}3 & 1 & 0 & 0 & 0\\ 0 & 0 & 0 & 0 & 0\end{bmatrix} + 40\begin{bmatrix}3 & 0 & 0 & 0 & 0\\ 0 & 1 & 0 & 0 & 0\end{bmatrix} + 120\begin{bmatrix}2 & 1 & 0 & 0 & 0\\ 1 & 0 & 0 & 0 & 0\end{bmatrix} + \\ & 120\begin{bmatrix}2 & 0 & 0 & 0 & 0\\ 1 & 1 & 0 & 0 & 0\end{bmatrix} + 120\begin{bmatrix}1 & 1 & 0 & 0 & 0\\ 2 & 0 & 0 & 0 & 0\end{bmatrix} + 120\begin{bmatrix}1 & 0 & 0 & 0 & 0\\ 2 & 1 & 0 & 0 & 0\end{bmatrix} + 40\begin{bmatrix}0 & 1 & 0 & 0 & 0\\ 3 & 0 & 0 & 0 & 0\end{bmatrix} + \\ & 40\begin{bmatrix}0 & 0 & 0 & 0 & 0\\ 3 & 1 & 0 & 0 & 0\end{bmatrix} + 80\begin{bmatrix}2 & 0 & 1 & 0 & 0\\ 0 & 0 & 0 & 0 & 0\end{bmatrix} + 80\begin{bmatrix}2 & 0 & 0 & 0 & 0\\ 0 & 0 & 1 & 0 & 0\end{bmatrix} + 160\begin{bmatrix}1 & 0 & 1 & 0 & 0\\ 1 & 0 & 0 & 0 & 0\end{bmatrix} + \\ & 160\begin{bmatrix}1 & 0 & 0 & 0 & 0\\ 1 & 0 & 1 & 0 & 0\end{bmatrix} + 80\begin{bmatrix}0 & 0 & 1 & 0 & 0\\ 2 & 0 & 0 & 0 & 0\end{bmatrix} + 80\begin{bmatrix}0 & 0 & 0 & 0 & 0\\ 2 & 0 & 1 & 0 & 0\end{bmatrix} - 160\begin{bmatrix}0 & 1 & 1 & 0 & 0\\ 0 & 0 & 0 & 0 & 0\end{bmatrix} - \\ & 160\begin{bmatrix}0 & 1 & 0 & 0 & 0\\ 0 & 0 & 1 & 0 & 0\end{bmatrix} - 160\begin{bmatrix}0 & 0 & 1 & 0 & 0\\ 0 & 1 & 0 & 0 & 0\end{bmatrix} - 160\begin{bmatrix}0 & 0 & 0 & 0 & 0\\ 0 & 1 & 1 & 0 & 0\end{bmatrix} - 384\begin{bmatrix}0 & 0 & 0 & 0 & 1\\ 0 & 0 & 0 & 0 & 0\end{bmatrix} - \\ & 384\begin{bmatrix}0 & 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0 & 1\end{bmatrix}\Big\} \end{aligned}$$

The expression thus obtained above for the G_1 representation generates the character values in that the coefficients of the various matrix types when sorted out according to the order of the conjugacy classes in Table 1 gives the character values multiplied by the order of the corresponding conjugacy class with the order of the group (3840) factored out. Consequently, the following string of coefficients is obtained after dividing the coefficients in the above expression by the order of each conjugacy class:

$$\{4\ 4\ 4\ 4\ 4\ 4\ 2\ 2\ 2\ 2\ 2\ 2\ 2\ 2\ 1\ 1\ 1\ 1\ 1\ 1\ 0\ 0\ 0\ 0\ 0\ 0\ 0\ 0\ 0\ 0 -1 -1 -1 -1 -1 -1\}$$

This string yields the character vales for the G_1 representation. In this manner, we obtain the character string for all 36 representations shown in Table 2. This of course involves considerable algebraic manipulations for all 36 irreducible representations, and all of these character values were computed manually. The character table thus constructed is shown in Table 3.

As can be seen from Table 3, the character table of $S_5[S_2]$ or G_{3840} contains 36 irreducible representations. There are four one-dimensional, four four-dimensional, eight five-dimensional, two six-dimensional, ten 10-dimensional, four 15-dimensional, and four 20-dimensional irreducible representations in the group which satisfy

$$4 \times 1^2 + 4 \times 4^2 + 8 \times 5^2 + 2 \times 6^2 + 10 \times 10^2 + 4 \times 15^2 + 4 \times 20^2 = 3840$$

The above condition is a requirement of the great orthogonality theorem. Moreover, we have ensured that all of the character values of 36 irreducible representations are orthogonal to each other by a computer code. This exhaustive checks involved 630 pairs of checks, and all of these checks produced correct zero overlaps for the irreducible representations shown in Table 3 confirming that the numbers are correct. Another important check is that the sum of squares of numbers multiplied by the corresponding orders of conjugacy classes in any row should add up to 3840. This result was also used to verify the correctness of all numbers in Table 3. All of these facts aid to confirm that the numbers in Table 3 are correct.

3. Nuclear Spin Statistics and Tunneling Splittings of Rotational/Rovibronic Levels and of $(H_2O)_5$ from Semirigid to Fully Nonrigid Limits

We consider the use of the character table for the water pentamer in the fully nonrigid limit. Liu et al.[8] have obtained vibrational-rotation-tunneling spectra of the deuterated water pentamer, $(D_2O)_5$. In its deuterated form, the cluster behaves as a quasi-planar oblate top with an averaged C_{5h} symmetry. We call this a semirigid structure in that the equilibrium geometry of the completely rigid structure, which is shown in Figure 1, is of C_1 symmetry and it's chiral. The tunneling motions in the deuterated form in the ground state are restricted to certain pseudorotations, which yield an overall averaged symmetry of C_{5h} or a G_{10} molecular symmetry group as noted by Liu et al.[8] For the fully protonated form, quantum tunneling among all 32 possible minima that arise from the flipping of the hydrogen atoms which yield $2^5 = 32$ permutations has been observed. Thus, we provide complete analysis of the rotational levels, tunneling splittings, and nuclear spin statistical weights of the rovibronic levels in both the semirigid and fully nonrigid wreath product group limits of $(H_2O)_5$.

Table 4 shows the correlation of the rotational levels of the pentamer in both the semirigid and nonrigid groups. Note that, the fully rigid structure (Figure 1) has only C_1 symmetry, and thus, all of the irreducible representations of the nonrigid group will correlate into the rigid structure. Moreover, it is highly unlikely that the cluster will retain its rigid C_1 geometry in view of quantum tunneling. Liu et al.[8] have contrasted the parts of the degenerate representation E_1 and E_2 in the C_{5h} symmetry, since the accidental degeneracies may be split by Corriolis coupling. However, for the analysis of nuclear spin statistical weights or the tunneling splittings, it is not necessary to make the distinction between the degenerate parts of the E_1 and E_2

TABLE 3: Character Table of the $S_5[S_2]$ Group with 36 Irreducible Reps

	1^{10}	1^82	1^62^2	1^42^3	1^22^4	2^5	1^62^2	1^64	1^42^3	1^424	1^22^4	1^22^24	2^5	2^34	1^43^2	1^46	1^223^2	1^226
	1	5	10	10	5	1	20	20	60	60	60	60	20	20	80	80	160	160
A_1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
A_2	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1	−1	−1	1	1	1	1
A_3	1	−1	1	−1	1	−1	1	−1	−1	1	1	−1	−1	1	1	−1	−1	1
A_4	1	−1	1	−1	1	−1	−1	1	1	−1	−1	1	1	−1	1	−1	−1	1
G_1	4	4	4	4	4	4	2	2	2	2	2	2	2	2	1	1	1	1
H_1	5	5	5	5	5	5	1	1	1	1	1	1	1	1	−1	−1	−1	−1
I_1	6	6	6	6	6	6	0	0	0	0	0	0	0	0	0	0	0	0
H_2	5	5	5	5	5	5	−1	−1	−1	−1	−1	−1	−1	−1	−1	−1	−1	−1
G_2	4	4	4	4	4	4	−2	−2	−2	−2	−2	−2	−2	−2	1	1	1	1
G_3	4	−4	4	−4	4	−4	2	−2	−2	2	2	−2	−2	2	1	−1	−1	1
H_3	5	−5	5	−5	5	−5	1	−1	−1	1	1	−1	−1	1	−1	1	1	−1
I_2	6	−6	6	−6	6	−6	0	0	0	0	0	0	0	0	0	0	0	0
H_4	5	−5	5	−5	5	−5	−1	1	1	−1	−1	1	1	−1	−1	1	1	−1
G_4	4	−4	4	−4	4	−4	−2	2	2	−2	−2	2	2	−2	1	−1	−1	1
H_5	5	3	1	−1	−3	−5	3	3	1	1	−1	−1	−3	−3	2	2	0	0
R_1	15	9	3	−3	−9	−15	3	3	1	1	−1	−1	−3	−3	0	0	0	0
M_1	10	6	2	−2	−6	−10	0	0	0	0	0	0	0	0	−2	−2	0	0
R_2	15	9	3	−3	−9	−15	−3	−3	−1	−1	1	1	3	3	0	0	0	0
H_6	5	3	1	−1	−3	−5	−3	−3	−1	−1	1	1	3	3	2	2	0	0
H_7	5	−3	1	1	−3	5	3	−3	−1	1	−1	1	3	−3	2	−2	0	0
R_3	15	−9	3	3	−9	15	3	−3	−1	1	−1	1	3	−3	0	0	0	0
M_2	10	−6	2	2	−6	10	0	0	0	0	0	0	0	0	−2	2	0	0
R_4	15	−9	3	3	−9	15	−3	3	1	−1	1	−1	−3	3	0	0	0	0
H_8	5	−3	1	1	−3	5	−3	3	1	−1	1	−1	−3	3	2	−2	0	0

	3^22^2	2^26	1^22^4	2^5	1^22^24	2^34	1^24^2	24^2	1^24^2	1^28	24^2	2 8	2^23^2	2^26	4 3^2	4 6	5^2	10
	80	80	60	60	120	120	60	60	240	240	240	240	160	160	160	160	384	384
A_1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
A_2	1	1	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1	−1	−1	1	1
A_3	1	−1	1	−1	−1	1	1	−1	1	−1	−1	1	1	−1	−1	1	1	−1
A_4	1	−1	1	−1	−1	1	1	−1	−1	1	1	−1	−1	1	1	−1	1	−1
G_1	1	1	0	0	0	0	0	0	0	0	0	0	−1	−1	−1	−1	−1	−1
H_1	−1	−1	1	1	1	1	1	1	−1	−1	−1	−1	1	1	1	1	0	0
I_1	0	0	−2	−2	−2	−2	−2	−2	0	0	0	0	0	0	0	0	1	1
H_2	−1	−1	1	1	1	1	1	1	1	1	1	1	−1	−1	−1	−1	0	0
G_2	1	1	0	0	0	0	0	0	0	0	0	0	1	1	1	1	−1	−1
G_3	1	−1	0	0	0	0	0	0	0	0	0	0	−1	1	1	−1	−1	1
H_3	−1	1	1	−1	−1	1	1	−1	−1	1	1	−1	1	−1	−1	1	0	0
I_2	0	0	−2	2	2	−2	−2	2	0	0	0	0	0	0	0	0	1	−1
H_4	−1	1	1	−1	−1	1	1	−1	1	−1	−1	1	−1	1	1	−1	0	0
G_4	1	−1	0	0	0	0	0	0	0	0	0	0	1	−1	−1	1	−1	1
H_5	−2	−2	1	−1	1	−1	1	−1	1	1	−1	−1	0	0	0	0	0	0
R_1	0	0	−1	1	−1	1	−1	1	−1	−1	1	1	0	0	0	0	0	0
M_1	2	2	2	−2	2	−2	2	−2	0	0	0	0	0	0	0	0	0	0
R_2	0	0	−1	1	−1	1	−1	1	1	1	−1	−1	0	0	0	0	0	0
H_6	−2	−2	1	−1	1	−1	1	−1	−1	−1	1	1	0	0	0	0	0	0
H_7	−2	2	1	1	−1	−1	1	1	1	−1	1	−1	0	0	0	0	0	0
R_3	0	0	−1	−1	1	1	−1	−1	−1	1	−1	1	0	0	0	0	0	0
M_2	2	−2	2	2	−2	−2	2	2	0	0	0	0	0	0	0	0	0	0
R_4	0	0	−1	−1	1	1	−1	−1	1	−1	1	−1	0	0	0	0	0	0
H_8	−2	2	1	1	−1	−1	1	1	−1	1	1	−1	0	0	0	0	0	0

	1^{10}	1^82	1^62^2	1^42^3	1^22^4	2^5	1^62^2	1^64	1^42^3	1^424	1^22^4	1^22^24	2^5	2^34	1^43^2	1^46	1^223^2	1^226
	1	5	10	10	5	1	20	20	60	60	60	60	20	20	80	80	160	160
M_3	10	2	−2	−2	2	10	4	2	0	−2	0	−2	4	2	1	1	−1	−1
W_1	20	4	−4	−4	4	20	2	−2	2	−2	2	−2	2	−2	−1	−1	1	1
M_4	10	2	−2	−2	2	10	−2	−4	2	0	2	0	−2	−4	1	1	−1	−1
M_5	10	2	−2	−2	2	10	2	4	−2	0	−2	0	2	4	1	1	−1	−1
W_2	20	4	−4	−4	4	20	−2	2	−2	2	−2	2	−2	2	−1	−1	1	1
M_6	10	2	−2	−2	2	10	−4	−2	0	2	0	2	−4	−2	1	1	−1	−1
M_7	10	−2	−2	2	2	−10	4	−2	0	−2	0	2	−4	2	1	−1	1	−1
W_3	20	−4	−4	4	4	−20	2	2	−2	−2	2	2	−2	−2	−1	1	−1	1
M_8	10	−2	−2	2	2	−10	−2	4	−2	0	2	0	2	−4	1	−1	1	−1
M_9	10	−2	−2	2	2	−10	2	−4	2	0	−2	0	−2	4	1	−1	1	−1
W_4	20	−4	−4	4	4	−20	−2	−2	2	2	−2	−2	2	2	−1	1	−1	1
M_{10}	10	−2	−2	2	2	−10	−4	2	0	2	0	−2	4	−2	1	−1	1	−1

TABLE 3 (Continued)

	$\frac{3^22^2}{80}$	$\frac{2^26}{80}$	$\frac{1^22^4}{60}$	$\frac{2^5}{60}$	$\frac{1^22^24}{120}$	$\frac{2^34}{120}$	$\frac{1^24^2}{60}$	$\frac{24^2}{60}$	$\frac{1^24^2}{240}$	$\frac{1^28}{240}$	$\frac{24^2}{240}$	$\frac{2\,8}{240}$	$\frac{2^23^2}{160}$	$\frac{2^26}{160}$	$\frac{43^2}{160}$	$\frac{46}{160}$	$\frac{5^2}{384}$	$\frac{10}{384}$
M_3	1	1	2	2	0	0	−2	−2	0	0	0	0	1	1	−1	−1	0	0
W_1	−1	−1	0	0	0	0	0	0	0	0	0	0	−1	−1	1	1	0	0
M_4	1	1	−2	−2	0	0	2	2	0	0	0	0	1	1	−1	−1	0	0
M_5	1	1	−2	−2	0	0	2	2	0	0	0	0	−1	−1	1	1	0	0
W_2	−1	−1	0	0	0	0	0	0	0	0	0	0	1	1	−1	−1	0	0
M_6	1	1	2	2	0	0	−2	−2	0	0	0	0	−1	−1	1	1	0	0
M_7	1	−1	2	−2	0	0	−2	2	0	0	0	0	1	−1	1	−1	0	0
W_3	−1	1	0	0	0	0	0	0	0	0	0	0	−1	1	−1	1	0	0
M_8	1	−1	−2	2	0	0	2	−2	0	0	0	0	1	−1	1	−1	0	0
M_9	1	−1	−2	2	0	0	2	−2	0	0	0	0	−1	1	−1	1	0	0
W_4	−1	1	0	0	0	0	0	0	0	0	0	0	1	−1	1	−1	0	0
M_{10}	1	−1	2	−2	0	0	−2	2	0	0	0	0	−1	1	−1	1	0	0

TABLE 4: Tunneling Splittings of Rotational Levels to the Semirigid to Fully Nonrigid $(H_2O)_5$

K	semirigid (C_{5h})	nonrigid ($S_5[S_2]$)
0	A_1	$A_1 + A_2 + A_3 + A_4 + H_1 + H_2 + H_3 + H_4 + H_5 + H_6 + H_7 + H_8 + 2I_1 + 2I_2 + 2M_1 + 2M_2 + 2M_3 + 2M_4 + 2M_5 + 2M_6 + 2M_7 + 2M_8 + 2M_9 + 2M_{10} + 3R_1 + 3R_2 + 3R_3 + 3R_4 + 4W_1 + 4W_2 + 4W_3 + 4W_4$
1	$A_1 + E_1$	$(A_1 + A_2 + A_3 + A_4 + H_1 + H_2 + H_3 + H_4 + H_5 + H_6 + H_7 + H_8 + 2I_1 + 2I_2 + 2M_1 + 2M_2 + 2M_3 + 2M_4 + 2M_5 + 2M_6 + 2M_7 + 2M_8 + 2M_9 + 2M_{10} + 3R_1 + 3R_2 + 3R_3 + 3R_4 + 4W_1 + 4W_2 + 4W_3 + 4W_4) + (G_1 + G_2 + G_3 + G_4 + H_1 + H_2 + H_3 + H_4 + H_5 + H_6 + H_7 + H_8 + I_1 + I_2 + 2M_1 + 2M_2 + 2M_3 + 2M_4 + 2M_5 + 2M_6 + 2M_7 + 2M_8 + 2M_9 + 2M_{10} + 3R_1 + 3R_2 + 3R_3 + 3R_4 + 4W_1 + 4W_2 + 4W_3 + 4W_4)$
2	$A_1 + E_1 + E_2$	$(A_1 + A_2 + A_3 + A_4 + H_1 + H_2 + H_3 + H_4 + H_5 + H_6 + H_7 + H_8 + 2I_1 + 2I_2 + 2M_1 + 2M_2 + 2M_3 + 2M_4 + 2M_5 + 2M_6 + 2M_7 + 2M_8 + 2M_9 + 2M_{10} + 3R_1 + 3R_2 + 3R_3 + 3R_4 + 4W_1 + 4W_2 + 4W_3 + 4W_4) + 2(G_1 + G_2 + G_3 + G_4 + H_1 + H_2 + H_3 + H_4 + H_5 + H_6 + H_7 + H_8 + I_1 + I_2 + 2M_1 + 2M_2 + 2M_3 + 2M_4 + 2M_5 + 2M_6 + 2M_7 + 2M_8 + 2M_9 + 2M_{10} + 3R_1 + 3R_2 + 3R_3 + 3R_4 + 4W_1 + 4W_2 + 4W_3 + 4W_4)$
3	$A_1 + E_1 + 2E_2$	$(A_1 + A_2 + A_3 + A_4 + H_1 + H_2 + H_3 + H_4 + H_5 + H_6 + H_7 + H_8 + 2I_1 + 2I_2 + 2M_1 + 2M_2 + 2M_3 + 2M_4 + 2M_5 + 2M_6 + 2M_7 + 2M_8 + 2M_9 + 2M_{10} + 3R_1 + 3R_2 + 3R_3 + 3R_4 + 4W_1 + 4W_2 + 4W_3 + 4W_4) + 3(G_1 + G_2 + G_3 + G_4 + H_1 + H_2 + H_3 + H_4 + H_5 + H_6 + H_7 + H_8 + I_1 + I_2 + 2M_1 + 2M_2 + 2M_3 + 2M_4 + 2M_5 + 2M_6 + 2M_7 + 2M_8 + 2M_9 + 2M_{10} + 3R_1 + 3R_2 + 3R_3 + 3R_4 + 4W_1 + 4W_2 + 4W_3 + 4W_4)$
4	$A_1 + 2E_1 + 2E_2$	$(A_1 + A_2 + A_3 + A_4 + H_1 + H_2 + H_3 + H_4 + H_5 + H_6 + H_7 + H_8 + 2I_1 + 2I_2 + 2M_1 + 2M_2 + 2M_3 + 2M_4 + 2M_5 + 2M_6 + 2M_7 + 2M_8 + 2M_9 + 2M_{10} + 3R_1 + 3R_2 + 3R_3 + 3R_4 + 4W_1 + 4W_2 + 4W_3 + 4W_4) + 4(G_1 + G_2 + G_3 + G_4 + H_1 + H_2 + H_3 + H_4 + H_5 + H_6 + H_7 + H_8 + I_1 + I_2 + 2M_1 + 2M_2 + 2M_3 + 2M_4 + 2M_5 + 2M_6 + 2M_7 + 2M_8 + 2M_9 + 2M_{10} + 3R_1 + 3R_2 + 3R_3 + 3R_4 + 4W_1 + 4W_2 + 4W_3 + 4W_4)$
5	$2A_1 + 2E_1 + 2E_2$	$2(A_1 + A_2 + A_3 + A_4 + H_1 + H_2 + H_3 + H_4 + H_5 + H_6 + H_7 + H_8 + 2I_1 + 2I_2 + 2M_1 + 2M_2 + 2M_3 + 2M_4 + 2M_5 + 2M_6 + 2M_7 + 2M_8 + 2M_9 + 2M_{10} + 3R_1 + 3R_2 + 3R_3 + 3R_4 + 4W_1 + 4W_2 + 4W_3 + 4W_4) + 4(G_1 + G_2 + G_3 + G_4 + H_1 + H_2 + H_3 + H_4 + H_5 + H_6 + H_7 + H_8 + I_1 + I_2 + 2M_1 + 2M_2 + 2M_3 + 2M_4 + 2M_5 + 2M_6 + 2M_7 + 2M_8 + 2M_9 + 2M_{10} + 3R_1 + 3R_2 + 3R_3 + 3R_4 + 4W_1 + 4W_2 + 4W_3 + 4W_4)$
n	$(A_1 + 2E_1 + 2E_2) + D^{n-5}$	$2(A_1 + A_2 + A_3 + A_4 + H_1 + H_2 + H_3 + H_4 + H_5 + H_6 + H_7 + H_8 + 2I_1 + 2I_2 + 2M_1 + 2M_2 + 2M_3 + 2M_4 + 2M_5 + 2M_6 + 2M_7 + 2M_8 + 2M_9 + 2M_{10} + 3R_1 + 3R_2 + 3R_3 + 3R_4 + 4W_1 + 4W_2 + 4W_3 + 4W_4) + 4(G_1 + G_2 + G_3 + G_4 + H_1 + H_2 + H_3 + H_4 + H_5 + H_6 + H_7 + H_8 + I_1 + I_2 + 2M_1 + 2M_2 + 2M_3 + 2M_4 + 2M_5 + 2M_6 + 2M_7 + 2M_8 + 2M_9 + 2M_{10} + 3R_1 + 3R_2 + 3R_3 + 3R_4 + 4W_1 + 4W_2 + 4W_3 + 4W_4) + D^{n-5}$

representations of the semirigid group, and it is suggested that the tunneling levels obtained using the correlation may be further contrasted according to other perturbations such as Corriolis coupling. Hence we do all our analysis of tunneling splittings in C_5 and $S_5[S_2]$ groups. In fact, the C_5 group is sufficient for the correlation of levels, as the horizontal plane does not generate any new permutation of the proton nuclei. As seen from Table 4, we obtain a pattern for the rotational levels into tunneling levels both in the semirigid and nonrigid limits. There is a period of 5 that arises from the symmetry of the semirigid molecule. A large number of tunneling levels arise for each of the rotational level in the fully nonrigid limit. However, as we show below, only a few of those levels are populated by nuclear spins for the protonic form of the pentamer although for the deuterated form more tunneling levels are populated.

Next we consider the nuclear spin statistics of the pentamer both in its protonated and deuterated forms. Following this we shall consider the correlation of rovibronic levels into tunneling levels together with the nuclear spin statistical weights. From the character table we can construct the combinatorial generating functions to enumerate the nuclear spin functions that transform according to the given irreducible representation. This information can be sorted out into nuclear spin multiplets from which we can derive the frequencies of various irreducible representations in all nuclear spin functions. Then we shall use the Pauli exclusion principle for the protons, which are fermions, and thus, the overall function must be antisymmetric. For the bosons such as deuterium nuclei, the overall function must be symmetric. Let us illustrate the technique with $(D_2O)_5$. Let us represent three m_s functions of the D nucleus by λ, μ, and ν, where these labels represent $m_s = -1$, 0, and +1, respectively. Let us consider the G_1 representation in character Table 3 for which we obtain the GGCI of the representation as

$$GF_{G_1} = \frac{1}{5!}\frac{1}{2^5}\{4{s_1}^{10} + 20{s_1}^8 s_2 + 40{s_1}^6{s_2}^2 + 40{s_1}^4{s_2}^3 + 20{s_1}^2{s_2}^4 + 4{s_2}^5 + 40{s_1}^6{s_2}^2 + 40{s_1}^6 s_4 + 120{s_1}^2{s_2}^3 + 120{s_1}^4 s_2 s_4 + 120{s_1}^2{s_2}^4 + 120{s_1}^2{s_2}^2 s_4 + 40{s_2}^5 + 40{s_2}^3 s_4 + 80{s_1}^4{s_3}^2 + 80{s_1}^4 s_6 + 160{s_1}^2{s_3}^2 s_2 + 160{s_1}^2 s_2 s_6 + 80{s_2}^2{s_3}^2 + 80{s_2}^2 s_6 - 160{s_2}^2{s_3}^2 - 160{s_2}^2 s_6 - 160 s_4{s_3}^2 - 160 s_4 s_6 - 384{s_5}^2 - 384 s_{10}\}$$

The ^{3}D nuclear spin generating function is obtained by replacing every s_k in the above expression by $(\lambda^k + \mu^k + \nu^k)$. Thus we obtain

$$P^{G_1} = \frac{1}{3840}[4(\lambda+\mu+\nu)^{10} + 20(\lambda+\mu+\nu)^8(\lambda^2+\mu^2+\nu^2) + 40(\lambda+\mu+\nu)^6(\lambda^2+\mu^2+\nu^2)^2 + 40(\lambda+\mu+\nu)^4(\lambda^2+\mu^2+\nu^2)^3 + 20(\lambda+\mu+\nu)^2(\lambda^2+\mu^2+\nu^2)^4 + 4(\lambda^2+\mu^2+\nu^2)^5 + 40(\lambda+\mu+\nu)^6(\lambda^2+\mu^2+\nu^2)^2 + 40(\lambda+\mu+\nu)^6(\lambda^4+\mu^4+\nu^4)^1 + 120(\lambda+\mu+\nu)^2(\lambda^2+\mu^2+\nu^2)^3 + 120(\lambda+\mu+\nu)^4(\lambda^2+\mu^2+\nu^2)(\lambda^4+\mu^4+\nu^4) + 120(\lambda+\mu+\nu)^2(\lambda^2+\mu^2+\nu^2)^4 + 120(\lambda+\mu+\nu)^2(\lambda^2+\mu^2+\nu^2)^2(\lambda^4+\mu^4+\nu^4) + 40(\lambda^2+\mu^2+\nu^2)^5 + 40(\lambda^2+\mu^2+\nu^2)^3(\lambda^4+\mu^4+\nu^4) + 80(\lambda+\mu+\nu)^4(\lambda^3+\mu^3+\nu^3)^2 + 80(\lambda+\mu+\nu)^4(\lambda^6+\mu^6+\nu^6) + 160(\lambda+\mu+\nu)^2(\lambda^2+\mu^2+\nu^2)(\lambda^3+\mu^3+\nu^3)^2 + 160(\lambda+\mu+\nu)^2(\lambda^2+\mu^2+\nu^2)(\lambda^6+\mu^6+\nu^6)\ 80(\lambda^2+\mu^2+\nu^2)^2(\lambda^3+\mu^3+\nu^3)^2 + 80(\lambda^2+\mu^2+\nu^2)^2(\lambda^6+\mu^6+\nu^6) - 160(\lambda^2+\mu^2+\nu^2)^2(\lambda^3+\mu^3+\nu^3)^2 - 160(\lambda^4+\mu^4+\nu^4)(\lambda^3+\mu^3+\nu^3)^2 - 160(\lambda^4+\mu^4+\nu^4)(\lambda^6+\mu^6+\nu^6) - 384(\lambda^5+\mu^5+\nu^5)^2 - 384(\lambda^{10}+\mu^{10}+\nu^{10})]$$

Once the above expression is simplified, the coefficient of a typical term $\lambda^i\mu^j\nu^k$ yields the number of ^{3}D nuclear spin functions containing i spin functions with $m_s = -1$, j functions with $m_s = 0$, and k spin functions with $m_s = +1$ that transform according to the G_2 irreducible representation. We sort the spin functions according to their total M_F nuclear spin quantum numbers which yield the various nuclear spin multiplets for $(D_2O)_5$ corresponding to the G_1 irreducible representation. We can obtain the corresponding results for the protonated form of water pentamer by replacing every s_k by $(\alpha^k + \beta^k)$ in the cycle index polynomial (above) for the G_2 representation. The results thus obtained are shown in Table 4 for both $(H_2O)_5$ and $(D_2O)_5$.

We can also obtain the total nuclear spin statistical weights from the nuclear spin species enumerated in Table 5. As seen from Table 5 and as expected, the proton nuclear spin multiplets occur with fewer frequencies as compared to the deuterium spin species. The nuclear spin statistical weights are obtained by first finding the frequencies of each of the irreducible representations. This is accomplished by multiplying the spin multiplicity by the frequency of each multiplet and then adding the all of the numbers. Consequently, we have obtained the frequencies of the various irreducible representations for the H and D nuclear spin functions as follows:

$$\Gamma_H = 21A_1 + 0A_2 + A_3 + 0A_4 + 24G_1 + 0G_2 + 0G_3 + 0G_4 + 15H_1 + 3H_2 + 0H_3 + 0H_4 + 15H_5 + 0H_6 + 3H_7 + 0H_8 + 6I_1 + 0I_2 + 6M_1 + 0M_2 + 10M_3 + 1M_4 + 0M_5 + 0M_6 + 6M_7 + 0M_8 + 3M_9 + 0M_{10} + 15R_1 + 3R_2 + 0R_3 + 0R_4 + 8W_1 + 0W_2 + 0W_3 + 0W_4$$

$$\Gamma_D = 252A_1 + 6A_2 + 21A_3 + 0A_4 + 504G_1 + 84G_2 + 24G_3 + 0G_4 + 420H_1 + 210H_2 + 15H_3 + 3H_4 + 378H_5 + 45H_6 + 90H_7 + 0H_8 + 336I_1 + 6I_2 + 315M_1 + 36M_2 + 336M_3 + 120M_4 + 168M_5 + 60M_6 + 210M_7 + 21M_8 + 150M_9 + 15M_{10} + 630R_1 + 315R_2 + 90R_3 + 18R_4 + 420W_1 + 210W_2 + 168W_3 + 120W_4$$

The overall nuclear spin statistical weights are obtained using the above frequencies and stipulating that the overall wave function must be antisymmetric for the fermions in compliance with the Pauli exclusion principle for $(H_2O)_5$. This means the overall wave function must transform as the A_3 irreducible representation for $(H_2O)_5$ in Table 3 which has the character values of −1 for all odd exchanges of nuclei. The nuclear spin statistical weights of the tunneling levels are thus obtained as A_1(1), A_2(0), A_3(21), A_4(0), G_1(0), G_2(0), G_3(24), G_4(0), H_1(0), H_2(0), H_3(15), H_4(3), H_5(3), H_6(0), H_7(15), H_8(0), I_1 (0), I_2(6), M_1(0), M_2(6), M_3(6), M_4(0), M_5(3), M_6(0), M_7(10), M_8(1), M_9 (0), M_{10}(0),R_1(0), R_2(0), R_3(15), R_4(3), W_1(0), W_2(0), W_3(8), and W_4(0). The nuclear spin statistical weights of the deuterated forms are obtained likewise with the exception that the overall wave function must be symmetric as $(D_2O)_5$ consists of bosons, and thus, the total wave function must transform as A_1. By using this together with the frequencies of the irreducible representations, we have obtained the nuclear spin statistical weights of the deuterated and protonated forms, which are shown in Table 6.

As noted by Liu et al.,[8] the VRT spectra exhibit averaged rotational constants that seem to fit into a semirigid psuedorotation model of $(D_2O)_5$. This corresponds to an averaged quasiplanar structure for $(D_2O)_5$ or a C_{5h} symmetry. Since D nuclei are heavier, all possible tunneling motions may not be feasible, and thus, we have also obtained the nuclear spin statistical weights and group theoretical tunneling analysis of both protonated and deuterated forms in the C_{5h} symmetry. Since the horizontal plane does not generate any new nuclear permutations of protons (deuterium nuclei), it suffices to analyze the nuclear spin statistical weights and tunneling splittings in the C_5 subgroup. If the weights are needed for each of the degenerate components of the E_1 and E_2 representations individually, the total weights are divided by 2. Thus, we have provided our analysis primarily in C_5 and further in fully nonrigid $S_5[S_2]$ groups.

Table 7 shows the correlation of the rovibronic levels from the semirigid C_{5h} symmetry to fully nonrigid $S_5[S_2]$ correlation

TABLE 5: Proton and Deuterium Spin Species of $(H_2O)_5$ and $(D_2O)_5$

sym	proton species	deuterium species	sym	proton species	deuterium
A_1	${}^{3}A_1(1)$, ${}^{7}A_1(1)$, ${}^{11}A_1(1)$	${}^{1}A_1(5)$ ${}^{5}A_1(7)$ ${}^{9}A_1(2)$ ${}^{11}A_1(6)$ ${}^{13}A_1(2)$ ${}^{15}A_1(4)$ ${}^{17}A_1(1)$	G_3	none	${}^{3}G_3(1)$ ${}^{5}G_3(1)$ ${}^{7}G_3(1)$ ${}^{9}G_3(1)$
A_2	none	${}^{1}A_2(1)$ ${}^{5}A_2(1)$	H_3	none	${}^{3}H_3(1)$ ${}^{5}H_3(1)$ ${}^{7}H_3(1)$
A_3	${}^{1}A_3$	${}^{3}A_3(1)$, ${}^{7}A_3(1)$ ${}^{11}A_3(1)$	I_2	none	${}^{1}I_2(1)$ ${}^{5}I_2(1)$
A_4	none	none	H_4	none	${}^{3}H_4(1)$
G_1	${}^{3}G_1$ ${}^{5}G_1$ ${}^{7}G_1$ ${}^{9}G_1$ ${}^{11}G_1$	${}^{1}G_1(4)$ ${}^{3}G_1(6)$ ${}^{5}G_1(12)$ ${}^{7}G_1(10)$ ${}^{9}G_1(11)$ ${}^{11}G_1(7)$ ${}^{13}G_1(6)$ ${}^{15}G_1(3)$ ${}^{17}G_1(2)$ ${}^{19}G_1(1)$	G_4	none	none
H_1	${}^{3}H_1$ ${}^{5}H_1$ ${}^{7}H_1$	${}^{1}H_1(5)$ ${}^{3}H_1(5)$ ${}^{5}H_1(12)$ ${}^{7}H_1(9)$ ${}^{9}H_1(11)$ ${}^{11}H_1(6)$ ${}^{13}H_1(5)$ ${}^{15}H_1(2)$ ${}^{17}H_1(1)$	H_5	${}^{1}H_5(1)$ ${}^{5}H_5(1)$ ${}^{9}H_5(1)$	${}^{3}H_5(9)$ ${}^{5}H_5(6)$ ${}^{7}H_5(10)$ ${}^{9}H_5(6)$ ${}^{11}H_5(7)$ ${}^{13}H_5(3)$ ${}^{15}H_5(3)$ ${}^{17}H_5(1)$ ${}^{19}H_5(1)$
I_1	${}^{1}I_1$ ${}^{5}I_1$	${}^{3}I_1(10)$ ${}^{5}I_1(7)$ ${}^{7}I_1(12)$ ${}^{9}I_1(6)$ ${}^{11}I_1(7)$ ${}^{13}I_1(2)$ ${}^{15}I_1(2)$	R_1	${}^{3}R_1$, ${}^{5}R_1$, ${}^{7}R_1$	${}^{1}R_1(4)$ ${}^{3}R_1(13)$ ${}^{5}R_1(17)$ ${}^{7}R_1(18)$ ${}^{9}R_1(14)$ ${}^{11}R_1(10)$ ${}^{13}R_1(6)$ ${}^{15}R_1(3)$ ${}^{17}R_1(1)$
H_2	${}^{3}H_2$	${}^{1}H_2(3)$ ${}^{3}H_2(4)$ ${}^{5}H_2(8)$ ${}^{7}H_2(6)$ ${}^{9}H_2(6)$ ${}^{11}H_2(3)$ ${}^{13}H_2(2)$	M_1	${}^{1}M_1$ ${}^{5}M_1$	${}^{1}M1(1)$ ${}^{3}M1(9)$ ${}^{5}M1(8)$ ${}^{7}M1(11)$ ${}^{9}M1(7)$ ${}^{11}M1(6)$ ${}^{13}M1(2)$ ${}^{15}M1(1)$
G_2	none	${}^{3}G_2(4)$ ${}^{5}G_2(3)$ ${}^{7}G_2(4)$ ${}^{9}G_2(2)$ ${}^{11}G_2(1)$	R_2	${}^{3}R_2$	${}^{1}R_2(5)$ ${}^{3}R_2(8)$ ${}^{5}R_2(13)$ ${}^{7}R_2(10)$ ${}^{9}R_2(9)$ ${}^{11}R_2(4)$ ${}^{13}R_2(2)$
H_6	none	${}^{1}H_6(1)$ ${}^{3}H_6(2)$ ${}^{5}H_6(3)$ ${}^{7}H_6(2)$ ${}^{9}H_6(1)$	M_5	none	${}^{3}M_5(6)$ ${}^{5}M_5(4)$ ${}^{7}M_5(6)$ ${}^{9}M_5(3)$ ${}^{11}M_5(3)$ ${}^{13}M_5(1)$ ${}^{15}M_5(1)$
H_7	${}^{3}H_7$	${}^{1}H_7(2)$ ${}^{3}H_7(1)$ ${}^{5}H_7(4)$ ${}^{7}H_7(2)$ ${}^{9}H_7(3)$ ${}^{11}H_7(1)$ ${}^{13}H_7(1)$	W_2	none	${}^{1}W_2(2)$ ${}^{3}W_2(7)$ ${}^{5}W_2(8)$ ${}^{7}W_2(8)$ ${}^{9}W_2(5)$ ${}^{11}W_2(3)$ ${}^{13}W_2(1)$
R_3	none	${}^{1}R_3(1)$ ${}^{3}R_3(4)$ ${}^{5}R_3(4)$ ${}^{7}R_3(4)$ ${}^{9}R_3(2)$ ${}^{11}R_3(1)$	M_6	none	${}^{1}M_6(2)$ ${}^{3}M_6(2)$ ${}^{5}M_6(4)$ ${}^{7}M_6(2)$ ${}^{9}M_6(2)$
M_2	none	${}^{1}M_2(2)$ ${}^{3}M_2(1)$ ${}^{5}M_2(3)$ ${}^{7}M_2(1)$ ${}^{9}M_2(1)$	M_7	${}^{1}M_7$ ${}^{5}M_7$	${}^{3}M_7(7)$ ${}^{5}M_7(5)$ ${}^{7}M_7(8)$ ${}^{9}M_7(4)$ ${}^{11}M_7(4)$ ${}^{13}M_7(1)$ ${}^{15}M_7(1)$
R_4	none	${}^{3}R_4(2)$ ${}^{5}R_4(1)$ ${}^{7}R_4(1)$	W_3	none	${}^{1}W_3(2)$ ${}^{5}W_3(6)$ ${}^{7}W_3(7)$ ${}^{9}W_3(6)$ ${}^{11}W_3(4)$ ${}^{13}W_3(2)$ ${}^{15}W_3(1)$
H_8	none	none	M_8	none	${}^{1}M_8(2)$ ${}^{5}M_8(2)$ ${}^{9}M_8(1)$
M_3	${}^{3}M_3$ ${}^{7}M_3$	${}^{1}M_3(6)$ ${}^{3}M_3(4)$ ${}^{5}M_3(12)$ ${}^{7}M_3(7)$ ${}^{9}M_3(9)$ ${}^{11}M_3(4)$ ${}^{13}M_3(4)$ ${}^{15}M_3(1)$ ${}^{17}M_3(1)$	M_9	${}^{3}M_9$	${}^{1}M_9(2)$ ${}^{3}M_9(4)$ ${}^{5}M_9(6)$ ${}^{9}M_9(5)$ ${}^{11}M_9(4)$ ${}^{13}M_9(2)$ ${}^{15}M_9(1)$
W_1	${}^{3}W_1$ ${}^{5}W_1$	${}^{1}W1(5)$ ${}^{3}W1(10)$ ${}^{5}W1(15)$ ${}^{7}W1(13)$ ${}^{9}W1(11)$ ${}^{11}W1(6)$ ${}^{13}W1(3)$ ${}^{15}W1(1)$	W_4	none	${}^{1}W_4(2)$ ${}^{3}W_4(5)$ ${}^{5}W_4(6)$ ${}^{7}W_4(5)$ ${}^{9}W_4(3)$ ${}^{11}W_4(1)$
M_4	${}^{1}M_4$	${}^{3}M_4(6)$ ${}^{5}M_4(4)$ ${}^{7}M_4(6)$ ${}^{9}M_4(2)$ ${}^{11}M_4(2)$	M_{10}	none	${}^{3}M_{10}(1)$ ${}^{5}M_{10}(1)$ ${}^{7}M_{10}(1)$

TABLE 6: Nuclear Spin Statistical Weights of $(H_2O)_5$ (^{2}H,^{3}D)

sym	nuclear spin statistical weights (H)[a]	nuclear spin weights (deuterared)[b]	sym	nuclear spin statistical weights (H)[a]	nuclear spin weights (deuterared)[b]
A_1	1	252	R_1	0	630
A_2	0	6	M_1	0	315
A_3	21	21	R_2	0	315
A_4	0	0	H_6	0	45
G_1	0	504	H_7	15	90
H_1	0	420	R_3	15	90
I_1	0	336	M_2	6	36
H_2	0	210	R_4	3	18
G_2	0	84	H_8	0	0
G_3	24	24	M_3	6	336
H_3	15	15	W_1	0	420
I_2	6	6	M_4	0	120
H_4	3	3	M_5	3	168
G_4	0	0	W_2	0	210
H_5	3	378	M_6	0	60
sym	**stat (H)**	**stat(D)**	**sym**	**stat (H)**	**stat(D)**
M_7	10	210	M_9	0	150
W_3	8	168	W_4	0	120
M_8	1	21	M_{10}	0	15

[a] Sum of (stat weights $\times$ dimension of reps) $= 2^{10}$. [a] Sum of (stat weights $\times$ dimension of reps) $= 3^{10}$.

of $(H_2O)_5$. Note that the correlation from the fully rigid chiral equilibrium structure with C_1 symmetry would involve every irreducible representation of the $S_5[S_2]$ nonrigid group and hence it is straightforward. The correlation table shown in Table 7 reveals that the A_1 rovibronic level is split into many tunneling levels. However, only some of the tunneling levels have nonzero nuclear spin statistical weights and would thus be populated. They are A_1, A_3, H_3, H_4, H_5, H_7, I_2, M_2, M_3, M_5, M_7, M_8, R_3, R_4, and W_3 tunneling levels, as seen from Table 7. Thus, primarily 15 tunneling levels have nonzero nuclear spin populations for $(H_2O)_5$ in its fully nonrigid ground state. The excited rovibronic states of $(H_2O)_5$ would of course have E_1 and E_2 symmetries that correlate according to the tunneling species in Table 7. Note that E_1 and E_2 representations have the same spin statistics and tunneling patterns owing to the accidental degeneracy of the 2 irreducible representations which yield the same cycle index polynomials. To observe nuclear spin multiplets, one needs much higher resolution spectra that have the capabilities to resolve hyperfine structural patterns. Such spectra are available on smaller clusters, and it is hoped that, in the future, hyperfine structures in higher clusters may become observable.

Wales and Walsh[32] have considered a group of 320 permutation-inversion operations for the water pentamer. These operations include only the single flip and bifurcation tunneling mechanisms as obtained on the basis of energetics of reaction pathways. This group when inversion operation is factored out becomes a group of order 160. It can be easily shown that this group of order 160 is the wreath product $C_5[S_2]$, which contains $(2!)^5 5 = 160$ operations. When the inversion operation is included, the group becomes the direct product $C_5[S_2] \times I$ and this contains 320 operations. The group $C_5[S_2]$ is a subgroup of $S_5[S_2]$. Thus, all of the results that we have obtained in the larger group, which is definitely more difficult to deal with,

TABLE 7: Correlation of Rovibronic Levels Semirigid $(H_2O)_5$ to Fully Nonrigid $(H_2O)_5$ with Nuclear Spin Statistical Weights in Parenthesis

semirigid(C_{5h})	nonrigid($S_5[S_2]$)
A_1(208)	$A_1(1) + A_2(0) + A_3(21) + A_4(0) + H_1(0) + H_2(0) + H_3(15) + H_4(3) + H_5(3) + H_6(0) + H_7(15) + H_8(0) + 2I_1(0) + 2I_2(6) + 2M_1(0) + 2M_2(6) + 2M_3(6) + 2M_4(0) + 2M_5(3) + 2M_6(0) + 2M_7(10) + 2M_8(1) + 2M_9(0) + 2M_{10}(0) + 3R_1(0) + 3R_2(0) + 3R_3(15) + 3R_4(3) + 4W_1(0) + 4W_2(0) + 4W_3(8) + 4W_4(0)$
E_1 (204)	$G_1(0) + G_2(0) + G_3(24) + G_4(0) + H_1(0) + H_2(0) + H_3(15) + H_4(3) + H_5(3) + H_6(0) + H_7(15) + H_8(0) + I_1(0) + I_2(6) + 2M_1(0) + 2M_2(6) + 2M_3(6) + 2M_4(0) + 2M_5(3) + 2M_6(0) + 2M_7(10) + 2M_8(1) + 2M_9(0) + 2M_{10}(0) + 3R_1(0) + 3R_2(0) + 3R_3(15) + 3R_4(3) + 4W_1(0) + 4W_2(0) + 4W_3(8) + 4W_4(0)$
E_2 (204)	$G_1(0) + G_2(0) + G_3(24) + G_4(0) + H_1(0) + H_2(0) + H_3(15) + H_4(3) + H_5(3) + H_6(0) + H_7(15) + H_8(0) + I_1(0) + I_2(6) + 2M_1(0) + 2M_2(6) + 2M_3(6) + 2M_4(0) + 2M_5(3) + 2M_6(0) + 2M_7(10) + 2M_8(1) + 2M_9(0) + 2M_{10}(0) + 3R_1(0) + 3R_2(0) + 3R_3(15) + 3R_4(3) + 4W_1(0) + 4W_2(0) + 4W_3(8) + 4W_4(0)$

can be subduced to the wreath product $C_5[S_2]$. Since the we have already illustrated the technique of subduction for the semirigid C_{5h} symmetry, we believe that this is straightforward application of group theory to obtain results in the $C_5[S_2]$ group from our results for the $S_5[S_2]$ group.

4. Conclusion

In this study, we have formulated the permutation group of $(H_2O)_5$ as the wreath product $S_5[S_2]$ with 3840 elements and its complete character table has been obtained for the first time. It was shown that the group has 36 conjugacy classes characterized by powerful matrix cycle types and 36 irreducible representations. The character values of the irreducible representations were obtained using powerful matrix-cycle type combinatorial generating functions. The character table thus constructed was used to generate the nuclear spin multiplets of both $(H_2O)_5$ and $(D_2O)_5$ using powerful generating functions. The tunneling splittings of the rotational levels were also obtained in the semirigid C_{5h} group and fully nonrigid $S_5[S_2]$ groups. We have shown that only 15 tunneling levels have nonzero nuclear spin statistical weights in the ground rovibronic state of $(H_2O)_5$. We have also obtained the correlation tables for all rotational and rovibronic levels of $(H_2O)_5$ by using the induced representation techniques. It was shown that more tunneling levels are obtained in the fully nonrigid limit of $(H_2O)_5$ compared to the quasi-planar C_{5h} model for the semirigid $(D_2O)_5$ which appears to exhibit restricted pseudorotation. It is hoped that the present study would stimulate further search for spectra with higher resolution that contain hyperfine features especially for $(H_2O)_5$.

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References and Notes

(1) Goldman, N.; Saykally, R. J. *J. Chem. Phys.* **2004**, *120*, 4777.
(2) Keutsch, F. N.; Saykally, R. J. *Proc. Natl. Acad. Sci,* **2001**, *98*, 10533.
(3) Dyke, T. R.; Muenter, J. S. *J. Chem. Phys.* **1972**, *57*, 5011.
(4) Dyke, T. R.; Mack, T. R.; Muenter, J. S. *J. Chem. Phys*. **1977**, *66*, 498.
(5) Fowler, J. E.; Schaefer, H. F., III. *J. Am. Chem. Soc*. **1995**, *117*, 446.
(6) Liu, K.; Cruzan, J. D.; Saykally, R. J. *Science* **1996**, *271*, 929.
(7) Saykally, R. J.; Blake, G. A. *Science* **1996**, *259*, 1570.
(8) Liu, K.; Brown, M. G.; Cruzan, J. D.; Saykally, R. J. *J. Phys. Chem.* **1997**, *101*, 9011.
(9) Cruzan, J. D.; Vinat, M. R.; Brown, M. G.; Lucas, D. D.; Liu, K.; Saykally, R. J. *Chem. Phys. Lett*. **1998**, *292*, 667.
(10) Puglianao, N.; Saykally, R. J. *J. Chem. Phys*. **1992**, *96*, 1832.
(11) Puglianao, N.; Saykally, R. J. *Science* **1992**, *257*, 1937.
(12) Dyke, T. R. *Topic. Curr. Chem*. **1983**, *120*, 85.
(13) Odutola, J. A.; Avis, A. I.; Curtis, C. W.; Dyke, T. R. *Mol. Phys*. **1981**, *42*, 267.
(14) Odutola, J. A.; Hu, T. A.; Prinslow, D.; Dyke, T. R. *J. Chem. Phys*. **1988**, *88*, 5352.
(15) Balasubramanian, K. *J. Chem. Phys*. **1991**, *95*, 8273.
(16) Longuet-Higgins, H. C. *Mol. Phys*. **1963**, *6*, 445.
(17) Balasubramanian, K. *J. Chem. Phys*. **1980**, *72*, 665.
(18) Balasubramanian, K. *Theor. Chim. Acta* **1990**, *78*, 31.
(19) Balasubramanian, K. *J. Chem. Phys*. **1981**, *74*, 6824.
(20) Balasubramanian, K. *J. Chem. Phys*. **1981**, *75*, 4572.
(21) Balasubramanian, K.; Dyke, T. R. *J. Phys. Chem*. **1984**, *88*, 4688.
(22) Balasubramanian, K. Symmetries and Properties of non-rigid Molecules. *Studies in Physical and Theoretical Chemistry*; Elsevier: Amsterdam, 1983; p 243.
(23) Balasubramanian, K. *Chem. Rev*. **1985**, *85*, 599.
(24) Balaban, A. T. *Chemical Applications of Graph Theory*; Academic Press: New York, 1976.
(25) King, R. B. *Inorg. Chem*. **1981**, *20*, 363.
(26) King, R. B. *Theor. Chim. Acta* **1981**, *59*, 25.
(27) Amar, F.; Kelman, M. E.; Berry, R. S. *J. Chem. Phys*. **1979**, *70*, 1973.
(28) Littlewood, D. E. *Theory of Group Representation and Matrix Product of Groups*; Clarendon Press: Oxford, 1940.
(29) Altmann, S. L.; Herzig, P. *Mol. Phys*. **1982**, *45*, 585. Altmann, S. L.; Herzig, P. *Point-Group Theory Tables*; Clarendon Press: Oxford, 1994.
(30) Hamermesh, M. *Group Theory And its Applications to Physical Problems*; Addison-Wesley: Reading, MA, 1964.
(31) Wales, D. J. *J. Chem. Phys*. **1999**, *111*, 8429.
(32) Wales, D. J.; Walsh, T. R. *J. Chem. Phys.* **1996**, *105*, 6957.
(33) Wales, D. J.; Walsh, T. R. *J. Chem. Phys*. **1997**, *106*, 7193.