In my Ph.D. thesis [66], I determined the character table of the MS group of a torsionally tunneling $Y_4X\text{-}XY_4$ molecule with two C_{4v} rotors. This group of 64 elements, G_{64}, is given in Table A12. This group is not the product of any smaller groups (i.e, it is not isomorphic with $C_{4v} \times C_{4v}$), and I determined the characters by laborious application of the character relations [67].

The molecular symmetry group of the hydrogen peroxide molecule is the $C_{2v}(M)$ group. Using it (see Table A2) we can determine that the species of the vibrational coordinates is

$$\Gamma(Q) = 3A_1 + 2B_2 \tag{80}$$

The double group of this molecule has recently been determined [70] and is needed for a separate symmetry classification of the rotational, torsional, and vibrational parts of the wavefunction. The selection rules can also be determined using the group. Molecules of this type are also discussed in Ref. [71]. The application of the molecular symmetry group to molecules in a solid matrix has been recently discussed by Miller and Decius [75].

V. SUMMARY

The total molecular Hamiltonian (in free space) can be written (neglecting translation) as the sum of nuclear-spin, rotational, vibrational, electron-orbital, and electron-spin parts plus a coupling term H'; that is:

$$\begin{aligned} H &= H^0_{ns} + H^0_r + H^0_v + H^0_{eo} + H^0_{es} + H' \\ &= H^0 + H' \end{aligned} \tag{81}$$

The eigenfunctions are then a zeroth-order product of nuclear-spin, rotational, vibrational, electron-orbital, and electron-spin parts plus a function correcting for the effect of H'; that is:

$$\begin{aligned}\psi &= \psi^0_{ns}\psi^0_r\psi^0_v\psi^0_{eo}\psi^0_{es} + \phi \\ &= \psi^0 + \phi \end{aligned} \tag{82}$$

Similarly the eigenvalues can be written as

$$\begin{aligned}E &= E^0_{ns} + E^0_r + E^0_v + E^0_{eo} + E^0_{es} + \Delta E \\ &= E^0 + \Delta E \end{aligned} \tag{83}$$

The elements of the Hamiltonian Group leave H, and the parts H^0_a (where "a" is ns, r, v, eo, or es) and H', invariant, and this group can be used to symmetry label the zeroth-order functions ψ^0_a and hence the functions ψ. The group to use for this purpose is the direct product of (a) the molecular symmetry group, (b) the external rotation group (giving the J,M labels), and (c) the electron permutation group. If we are not interested in the separate classification of ψ^0_{eo} and ψ^0_{es} (and we are generally not) then a sufficient symmetry labeling of the energy levels is obtained using J and the molecular symmetry group. The elements of the molecular symmetry group are nuclear permutations (i.e., the permutation of the spatial coordinates, momenta, and spins of identical nuclei) with or without inversion of the coordinates, and the MS group consists only of the feasible elements of the complete nuclear permutation group. The symmetry labels obtained using the MS group can be used to determine which E^0 are coupled by H', which are coupled by an external electric or magnetic field, and which are coupled by an electromagnetic radiation field. The latter results give us the selection rules for allowed transitions. This group is set up without knowing any of the details of H. Knowing the expressions for the zeroth-order Hamiltonians H^0_a we can construct a symmetry group for each based on a study of the coordinate transformations that leave each H^0_a invariant [79]. These symmetry groups neglect the effect of H' and will be near-symmetry groups of H. The point group is such a near-symmetry group obtained from

$H_v^0 + H_e^0$, and Coriolis coupling terms in H' spoil the symmetry labels. The four-group for an asymmetric top is obtained from H_r^0, and its symmetry classification can also be spoilt by Coriolis coupling terms in H'. For linear molecules and for molecules with two or more identical coaxial internal rotors (such as dimethylacetylene) an extended molecular symmetry group is needed in order to label the separate E_a^0, but the molecular symmetry group can be used to label the overall energy levels E.

We have been particularly concerned with labeling the rotation-vibration energy levels, and the four labels we attach are J, (vib), (rot), and Γ_{rv}(MS), where J is the total angular-momentum quantum number not including nuclear spin, (vib) is the vibrational quantum number label, (rot) is the label obtained from the internal rotation group, i.e., K (also ±ℓ or G[2]) for a symmetric top and A, B_a, B_b, or B_c (alternatively, ee, eo, oo, or oe, respectively) for an asymmetric top, and Γ_{rv}(MS) is the irreducible representation label from the MS group. The labels (vib) and (rot) are only perfectly good distinguishing labels for a rigid-rotor harmonic oscillator and are spoilt by anharmonicity, Coriolis coupling, and centrifugal distortion. The labels J and Γ_{rv}(MS) are good distinguishing labels since states having different J or Γ_{rv}(MS) are not mixed by H'_{rv} (we are neglecting nuclear hyperfine interactions and the breakdown of the Born-Oppenheimer approximation). Selection rules for perturbations or for transitions are quoted in terms of changes in these four labels, and while the rules on the changes of the labels (vib) or (rot) are often very restricting they can break down because of anharmonicity, Coriolis coupling, or centrifugal distortion. The rules on J and Γ_{rv}(MS) do not break down unless there is nuclear hyperfine interaction, in which case the useful labels become F and $\Gamma_{overall}$(MS).

The important result in the paper by Oka [68], is that the overall symmetry label $\Gamma_{overall}$(MS) in fact represents the overall parity label. For example, for H_2O the label $\Gamma_{overall}$(MS) is either B_1 or B_2 as the parity is - or +, and we could label the overall states (ψ) by parity rather than by $\Gamma_{overall}$(MS), since this is the fundamental reason for the distinction. For molecules for which E* is not feasible this is still true; A_1 overall states of CH_3F have "-" parity and A_2 overall states have "+" parity. This can easily be seen since $(12)\psi = -\psi$ by the Exclusion Principle, $(12)^*\psi = +\psi$ for A_1 and $-\psi$ for A_2 states and $E^* = (12)(12)^*$. It may be useful to label the rovibrational states (rotational levels) with an "incipient overall symmetry label" in parenthesis after Γ_{rv}(MS) in case there is a possibility of seeing nuclear hyperfine structure. We would then label the rovibrational states as Γ_{rv}(MS) [$\Gamma_{overall}$(MS)]. For water the rovibrational states would be labelled $A_1(B_2)$, $A_2(B_1)$, $B_1(B_1)$, and $B_2(B_2)$, or using + and - instead of $\Gamma_{overall}$(MS), $A_1(+)$, $A_2(-)$, $B_1(-)$, and $B_2(+)$. Similarly for CH_3F we have $A_1(A_1)$, $A_2(A_2)$, and $E(A_1 + A_2)$ or, as in [68], $A_1(-)$, $A_2(+)$, and $E(\pm)$. It is, however, necessary to use $\Gamma_{overall}$(MS) rather than parity for determining which nuclear spin state a particular rovibrational state can be in, and, therefore, for determining nuclear statistical weights. We should not view the <u>addition</u> of ± to Γ_{rv}(MS) as giving us any new information about the level, in the absence of nuclear hyperfine splittings, since it does not. More importantly we must not use ± <u>instead</u> of Γ_{rv}(MS) since by doing this we lose information; for example, ammonia has six possible Γ_{rv}(MS), i.e. A_1', A_2', E', A_1'', A_2'', and E'' (see Fig. 21), but using only parity, the first three would be + and the last three -, and some important distinctions are lost.

In this chapter I have concentrated on the determination of the symmetry labels for the rotational and vibrational states. The nuclear-spin states were also symmetry labeled for the purpose of determining the spin statistical weights. Electronic states can also be classified in the molecular symmetry group (although for linear molecules and molecules with identical coaxial internal rotors the extended molecular symmetry group is needed), and this symmetry should be considered when constructing electronic wavefunctions. The transformation properties of electronic wavefunctions written in terms of the xyz coordinates of the electrons can be determined once the transformation properties of the Euler angles have been determined. The transformation properties of LCAO wavefunctions are easy to determine under the effect of nuclear permutations and permutation inversions (and similar to the transformation of nuclear-spin wavefunctions) since the operations just permute the nuclear labels on the atomic orbitals.

One final point: We can determine J (or F) experimentally (from the number of Stark components) but can you think of a direct way of determining $\Gamma_{rv}(MS)$, or $\Gamma_{overall}(MS)$ (i.e., parity), by experiment?

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VI. TABLES

TABLE 1

The Effect of the Operations of the $C_{2v}(M)$ Group of H_2O on the Euler Angles Defined in Fig. 5 (The Axes are Defined in Fig. 4)

E	(12)	E*	(12)*
θ	$\pi - \theta$	$\pi - \theta$	θ
ϕ	$\phi + \pi$	$\phi + \pi$	ϕ
χ	$-\chi + \pi$	$-\chi$	$\chi + \pi$

TABLE 2

The Transformation Properties of Symmetric-Top Rotational Wavefunctions $|J,k_a,M>$ of H_2O in the $C_{2v}(M)$ Group. $K_a = |k_a|$

E	(12)	E*	(12)*
$\|J,K_a,M>$	$(-1)^J\|J,-K_a,M>$	$(-1)^{J-K_a}\|J,-K_a,M>$	$(-1)^{K_a}\|J,K_a,M>$
$\|J,-K_a,M>$	$(-1)^J\|J,K_a,M>$	$(-1)^{J+K_a}\|J,K_a,M>$	$(-1)^{K_a}\|J,-K_a,M>$
$\psi^+(J,K_a)$	$(-1)^J\psi^+(J,K_a)$	$(-1)^{J+K_a}\psi^+(J,K_a)$	$(-1)^{K_a}\psi^+(J,K_a)$
$\psi^-(J,K_a)$	$(-1)^{J+1}\psi^-(J,K_a)$	$(-1)^{J+K_a+1}\psi^-(J,K_a)$	$(-1)^{K_a}\psi^-(J,K_a)$

TABLE 3

The Symmetry Species of the + and - Combinations of K_a-Symmetric-Top Wavefunctions of H_2O as a Function of the Evenness and Oddness of J and K_a

	J even		J odd	
	K_a even	K_a odd	K_a even	K_a odd
$\Gamma[\psi^+(J,K_a)]$	A_1	A_2	B_1	B_2
$\Gamma[\psi^-(J,K_a)]$	B_1	B_2	A_1	A_2

TABLE 4

The Species of the + and - Combinations of K_c-Symmetric-Top Functions of H_2O as a Function of the Evenness and Oddness of J and K_c

	J even		J odd	
	K_c even	K_c odd	K_c even	K_c odd
$\Gamma[\psi^+(J,K_c)]$	A_1	B_1	B_2	A_2
$\Gamma[\psi^-(J,K_c)]$	B_2	A_2	A_1	B_1

TABLE 5

The Symmetry Species of the $J_{K_aK_c}$ Levels of H_2O as a Function of Evenness and Oddness of (K_a,K_c)

K_aK_c	Γ	Statist. Wt.
ee	A_1	1
oo	A_2	1
eo	B_1	3
oe	B_2	3

TABLE 6

The Determination of the Species of the Normal Coordinates of Water from the Cartesian Displacements ($xyz \equiv cab$)

	E	(12) or C_2	E* or $\sigma(yz)$	(12)* or $\sigma(xz)$	
	δx_1	$-\delta x_2$	$-\delta x_1$	δx_2	
	δx_2	$-\delta x_1$	$-\delta x_2$	δx_1	
	δx_3	$-\delta x_3$	$-\delta x_3$	δx_3	
	δy_1	$-\delta y_2$	δy_1	$-\delta y_2$	
	δy_2	$-\delta y_1$	δy_2	$-\delta y_1$	
	δy_3	$-\delta y_3$	δy_3	$-\delta y_3$	
	δz_1	δz_2	δz_1	δz_2	
	δz_2	δz_1	δz_2	δz_1	
	δz_3	δz_3	δz_3	δz_3	
Total	9	-1	3	1	
(μ_c)	T_x	$-T_x$	$-T_x$	T_x	B_1
(μ_a)	T_y	$-T_y$	T_y	$-T_y$	B_2
(μ_b)	T_z	T_z	T_z	T_z	A_1
(R_c)	R_x	$-R_x$	R_x	$-R_x$	B_2
(R_a)	R_y	$-R_y$	$-R_y$	R_y	B_1
(R_b)	R_z	R_z	$-R_z$	$-R_z$	A_2
	6	-2	0	0	
$\Gamma(Q)$	3	1	3	1	$2A_1 + B_2$

TABLE 7

The Transformation Properties of the Nuclear-Spin Wavefunctions of H_2O in the $C_{2v}(M)$ Group

E	(12)	E*	(12)*	Γ
$\alpha(1)\alpha(2)$	$\alpha(1)\alpha(2)$	$\alpha(1)\alpha(2)$	$\alpha(1)\alpha(2)$	A_1
$\alpha(1)\beta(2)$ $\beta(1)\alpha(2)$	$\beta(1)\alpha(2)$ $\alpha(1)\beta(2)$	$\alpha(1)\beta(2)$ $\beta(1)\alpha(2)$	$\beta(1)\alpha(2)$ $\alpha(1)\beta(2)$	$A_1 + B_2$
$\beta(1)\beta(2)$	$\beta(1)\beta(2)$	$\beta(1)\beta(2)$	$\beta(1)\beta(2)$	A_1

TABLE 8

The D_∞ Rotation Group for Symmetric-Top Molecules

k	Γ	E	C_∞^ϕ	•••	∞C_2
0 (J even)	Σ^+	1	1	•••	1
0 (J odd)	Σ^-	1	1	•••	-1
±1	Π	2	2 cos ϕ	•••	0
±2	Δ	2	2 cos 2ϕ	•••	0
±3	Φ	2	2 cos 3ϕ	•••	0
±4	Γ	2	2 cos 4ϕ	•••	0
•••	•••	•••	•••	•••	•••
•••	•••	•••	•••	•••	•••
•••	•••	•••	•••	•••	•••

TABLE 9

The Transformation Properties of the Euler Angles of CH_3F in its MS Group

E	(123)	(12)*
θ	θ	$\pi - \theta$
ϕ	ϕ	$\phi + \pi$
χ	$\chi - 2\pi/3$	$4\pi/3 - \chi$

TABLE 10

The Transformation Properties of the Symmetric-Top Rotational Wavefunctions of CH_3F in the $C_{3v}(M)$ Group[a]

E	(123)	(12)*
$\|J,K,M\rangle$	$\omega^{2K}\|J,K,M\rangle$	$(-1)^{J-K}\omega^{2K}\|J,-K,M\rangle$
$\|J,-K,M\rangle$	$\omega^{K}\|J,-K,M\rangle$	$(-1)^{J+K}\omega^{K}\|J,K,M\rangle$

[a] $\omega = \exp(2\pi i/3)$ and $\omega + \omega^2 = -1$.

TABLE 11

The Symmetry Classification of the Rotational Wavefunctions of CH_3F in the $C_{3v}(M)$ Group[a]

K	Γ	Statist. Wt.
0 (J even)	A_1	4
0 (J odd)	A_2	4
3n ± 1	E	4
3n	$A_1 + A_2$	8

[a] n is integral

TABLE 12

The Transformation Properties of the Internal Coordinates of CH_3F and of the Redundant Coordinate R of Eq. (27)

	E	(123)	(12)*	
	δr_1	δr_3	δr_2	
	δr_2	δr_1	δr_1	
	δr_3	δr_2	δr_3	
	δr_4	δr_4	δr_4	
	$\delta\alpha_1$	$\delta\alpha_3$	$\delta\alpha_2$	
	$\delta\alpha_2$	$\delta\alpha_1$	$\delta\alpha_1$	
	$\delta\alpha_3$	$\delta\alpha_2$	$\delta\alpha_3$	
	$\delta\beta_1$	$\delta\beta_3$	$\delta\beta_2$	
	$\delta\beta_2$	$\delta\beta_1$	$\delta\beta_1$	
	$\delta\beta_3$	$\delta\beta_2$	$\delta\beta_3$	
	10	1	4	$4A_1 + 3E$
$\Gamma(R)$	1	1	1	A_1
$\Gamma(Q)$	9	0	3	$3A_1 + 3E$

TABLE 13

The Transformation Properties of the Proton Nuclear-Spin States of CH_3F

E	(123)	(12)*	Γ
ααα	ααα	ααα	A_1
ααβ	βαα	ααβ	$A_1 + E$
αβα	ααβ	βαα	
βαα	αβα	αβα	
αββ	βαβ	βαβ	$A_1 + E$
ββα	αββ	ββα	
βαβ	ββα	αββ	
βββ	βββ	βββ	A_1

TABLE 14

The Transformation Properties of the Euler Angles of CO_2 in the $D_{\infty h}$(EM) Group

	E_ε	E_ε^*	$(p)_\varepsilon^*$	$(p)_\varepsilon$
θ	θ	$\pi - \theta$	θ	$\pi - \theta$
ϕ	ϕ	$\phi + \pi$	ϕ	$\phi + \pi$
χ'	$\chi' - \varepsilon$	$-\chi' - \varepsilon$	$\pi + \chi' - \varepsilon$	$\pi - \chi' - \varepsilon$

TABLE 15

The Species of the Rotational Wavefunctions of a Linear Molecule in the $D_{\infty h}$(EM) Group

ℓ		$\Gamma(\psi_{J\ell M})$
0	J even	Σ_g^+
	J odd	Σ_g^-
±1		Π_g
±2		Δ_g
±3		Φ_g
...		...

TABLE 16

The Species of the Skeletal-Bending Wavefunctions of CO_2 as a Function of the Quantum Number ℓ

ℓ	$\Gamma(\psi_{v_2,\ell})$
0	Σ_g^+
±1	Π_u
±2	Δ_g
±3	Φ_u
...	...

TABLE 17

Symmetry Restrictions on Rocontortional Transitions for all Symmetry Types of Vibrational Transition of the C_{2v}(M) Molecule XH_2. The Bracketed Transitions are Forbidden

$\Gamma_v'' \times \Gamma_v'$	$\Gamma_c'' \times \Gamma_c'$	$\Gamma_r'' \times \Gamma_r'$
A_1	A_1	A_2
	B_2	B_1
A_2	A_1	(A_1)
	B_2	B_2
B_1	A_1	B_2
	B_2	(A_1)
B_2	A_1	B_1
	B_2	A_2

TABLE 18

Symmetry-Derived Selection Rules on v_c, K_a, and K_c for all Symmetry Types of Vibrational Transition in the $C_{2v}(M)$ Group. The Rule $\Delta J = 0, \pm 1$ is Understood. The Bracketed Transitions are Forbidden in the Absence of Coriolis Coupling for the Unsymmetric XH_2 Molecule

$\Gamma_v'' \times \Gamma_v'$	Δv_c	ΔK_a	ΔK_c
A_1	even	odd	odd
	odd	even	odd
A_2	even	(even)	(even)
	odd	odd	even
B_1	even	odd	even
	odd	(even)	(even)
B_2	even	even	odd
	odd	odd	odd

TABLE 19

The Transformation Properties of the Euler Angles and of the Symmetric-Top Rotational Wavefunctions for NH_3[a]

	E	(123)	(12)	E*	(123)*	(12)*
	θ	θ	$\pi - \theta$	θ	θ	$\pi - \theta$
	ϕ	ϕ	$\phi + \pi$	ϕ	ϕ	$\phi + \pi$
	χ	$\chi - 2\pi/3$	$-\chi + \pi/3$	$\chi + \pi$	$\chi + \pi/3$	$-\chi + 4\pi/3$
	$\|JKM\rangle$	$\lambda^{4K}\|JKM\rangle$	$(-1)^{J-K}\lambda^{K}\|J\text{-}KM\rangle$	$(-1)^{K}\|JKM\rangle$	$\lambda^{K}\|JKM\rangle$	$(-1)^{J-K}\lambda^{4K}\|J\text{-}KM\rangle$
$\Gamma_{rot}(K = 0)$	1	1	$(-1)^J$	1	1	$(-1)^J$
$\Gamma_{rot}(K \neq 0)$	2	$\lambda^{2K} + \lambda^{4K}$	0	$2(-1)^K$	$\lambda^{K} + \lambda^{5K}$	0

[a] $\lambda = \exp(\pi i/3)$, $\lambda^6 = +1$, $\lambda^3 = -1$, $\lambda^2 + \lambda^4 = -1$, $\lambda + \lambda^5 = +1$

TABLE 20

Symmetry Species of Rotational Wavefunctions of Ammonia in the D_{3h}(M) Group[a]

K		Γ_{rot}	Statist. Wt.
0	J even	A_1'	0
	J odd	A_2'	4
6n ± 1		E''	2
6n ± 2		E'	2
6n ± 3		$A_1'' + A_2''$	4
6n		$A_1' + A_2'$	4

[a] Where n is integral

TABLE 21

The Transformation Properties of the Euler Angles θ, ϕ, χ (a axis defined by θ and ϕ) and the Torsional Angle α of Methanol in the C_{3v}(M) Group

E	(123)	(12)*
θ	θ	$\pi - \theta$
ϕ	ϕ	$\phi + \pi$
χ	χ	$-\chi$
α	$\alpha - 2\pi/3$	$4\pi/3 - \alpha$

TABLE 22

The Species of the Rotational Wavefunctions of Methanol in the $C_{3v}(M)$ Group

K_aK_c	Γ_{rot}
ee	A_1
oo	A_2
eo	A_2
oe	A_1

TABLE 23

The Species of the Torsional Wavefunctions of Methanol in the $C_{3v}(M)$ Group[a]

$\|m\|$	Γ_{tor}
0	A_1
$3n \pm 1$	E
$3n$	$A_1 + A_2$

[a] n is integral

TABLE 24

The Transformation Properties of the In-Plane and Out-of-Plane Perpendicular C-H Stretching Coordinates of Methanol

E	(123)	(12)*
δr_1	δr_3	δr_2
δr_2	δr_1	δr_1
δr_3	δr_2	δr_3
α	$\alpha - 2\pi/3$	$4\pi/3 - \alpha$
$\delta r_1 \cos\alpha$	$\delta r_3 \cos(\alpha - 2\pi/3)$	$\delta r_2 \cos(4\pi/3 - \alpha)$
$\delta r_2 \cos(\alpha + 2\pi/3)$	$\delta r_1 \cos\alpha$	$\delta r_1 \cos(6\pi/3 - \alpha)$
$\delta r_3 \cos(\alpha + 4\pi/3)$	$\delta r_2 \cos(\alpha + 2\pi/3)$	$\delta r_3 \cos(8\pi/3 - \alpha)$
$S^{(i)}$	$S^{(i)}$	$S^{(i)}$
$S^{(o)}$	$S^{(o)}$	$-S^{(o)}$

TABLE 25

The Transformation Properties of the Euler Angles θ, ϕ, χ and the Torsional Angles α_a and α_b under the Effect of the Generators of G_{36} for the Acetone Molecule

E	(123)	(456)	(23)(56)*	(14)(26)(35)(ab)*
θ	θ	θ	$\pi - \theta$	θ
ϕ	ϕ	ϕ	$\phi + \pi$	ϕ
χ	χ	χ	$-\chi$	$\chi + \pi$
α_a	$\alpha_a + 2\pi/3$	α_a	$-\alpha_a$	$-\alpha_b$
α_b	α_b	$\alpha_b + 2\pi/3$	$-\alpha_b$	$-\alpha_a$

TABLE 26

The Symmetry Species of the Rotational Wavefunctions of Acetone in the G_{36} Group and the C_{2v} Group

K_aK_c	$\Gamma(G_{36})$	$\Gamma(C_{2v})$
ee	A_1	A_1
oo	A_3	A_2
eo	A_2	B_1
oe	A_4	B_2

TABLE 27

The Species of the Torsional Wavefunction of Acetone

$$\psi_t = \exp(im_a\alpha_a)\exp(im_b\alpha_b)$$

	$(m_a + m_b)$		
$(m_a - m_b)$	0	3n ± 1	3n
0	A_1	E_3	$A_1 + A_3$
3n ± 1	E_1	G	$E_1 + E_2$
3n	$A_1 + A_2$	$E_3 + E_4$	$A_1 + A_2 + A_3 + A_4$

TABLE 28

Statistical Weights of the Rotorvibrational States of Acetone

Γ_{rtv}	Statist. Wt.
A_1	6
A_2	10
A_3	6
A_4	10
E_1	4
E_2	4
E_3	2
E_4	6
G	16

TABLE 29

Correlations of Rotorvibrational Levels for Acetone for Tunneling Between the Nine C_{2v} Conformations

C_{2v} level	G_{36} Sublevels
A_1	$A_1 + E_1 + E_3 + G$
A_2	$A_3 + E_2 + E_3 + G$
B_1	$A_2 + E_1 + E_4 + G$
B_2	$A_4 + E_2 + E_4 + G$

TABLE 30

The Species of the Lower Torsional Vibrational States of Rigid Acetone in the C_{2v} Group and the Tunneling Species in the G_{36} Group

v^+	v^-	$\Gamma(C_{2v})$	$\Gamma(G_{36})$
0	0	A_1	$A_1 + E_1 + E_3 + G$
1	0	A_2	$A_3 + E_2 + E_3 + G$
0	1	B_1	$A_2 + E_1 + E_4 + G$
2	0	A_1	$A_1 + E_1 + E_3 + G$
1	1	B_2	$A_4 + E_2 + E_4 + G$
0	2	A_1	$A_1 + E_1 + E_3 + G$
3	0	A_2	$A_3 + E_2 + E_3 + G$
2	1	B_1	$A_2 + E_1 + E_4 + G$
1	2	A_2	$A_3 + E_2 + E_3 + G$
0	3	B_1	$A_2 + E_1 + E_4 + G$

TABLE 31

Rotational-Torsional Selection Rules for the Vibrational Bands of Free-Rotor Acetone[a]

$\Gamma_v' \times \Gamma_v''$	$(\Delta K_a, \Delta K_c)$	$(\Delta m_a, \Delta m_b)$
A_1	(±1, ±1)	(0, 0)
A_2	(±1, 0)	(0, 0)
A_3	Inactive[a]	Inactive[a]
A_4	(0, ±1)	(0, 0)
G	(0, ±1),(±1, 0),(0, 0),(±1, ±1)	(0, ±1),(±1, 0)

[a] We neglect the weak symmetry-allowed transitions with ΔK_a, ΔK_c, Δm_a, or Δm_b larger than 1.

TABLE 32

The Transformation Properties of the Euler Angles of Dimethylacetylene for the Generators of G_{36}

E	(123)	(456)	(23)(56)*	(14)(26)(35)(ab)(cd)*
θ	θ	θ	$\pi - \theta$	θ
ϕ	ϕ	ϕ	$\phi + \pi$	ϕ
χ_a	$\chi_a - 2\pi/3$	χ_a	$-\chi_a$	$\chi_b + \pi$
χ_b	χ_b	$\chi_b + 2\pi/3$	$-\chi_b$	$\chi_a + \pi$

TABLE 33

The Symmetry Classification of the Rotation-Torsion Functions of Dimethylacetylene

	$k_a + k_b$		
$k_a - k_b$	0	$3n \pm 1$	$3n$
0	A_1 (J even) A_2 (J odd)	E_1	$A_1 + A_2$
$3n \pm 1$	E_3	G	$E_3 + E_4$
$3n$	$A_1 + A_3$ (J even) $A_2 + A_4$ (J odd)	$E_1 + E_2$	$A_1 + A_2 + A_3 + A_4$

TABLE 34

The Separate Classification of the Rotational and Torsional Wavefunctions of Dimethylacetylene in $G_{36}^{\dagger}$

K	Γ_{rot}	K_i	Γ_{tor}
0 J even	A_{1s}	0	A_{1s}
J odd	A_{2s}		
$6n \pm 2$	E_{1s}	$6n \pm 2$	E_{3s}
$6n \pm 1$	E_{2d}	$6n \pm 1$	E_{3d}
$6n$	$A_{1s} + A_{2s}$	$6n$	$A_{1s} + A_{3s}$
$6n \pm 3$	$A_{3d} + A_{4d}$	$6n \pm 3$	$A_{1d} + A_{3d}$

TABLE 35

The Selection Rules[a] on the Fundamentals of Dimethylacetylene Using the $G_{36}^{\dagger}$ Group

No.	Approximate description	Species	Selection Rules: Infrared ($\Delta J = 0, \pm 1$)	Selection Rules: Raman ($\Delta J = 0, \pm 1, \pm 2$)
1	C-H stretch	A_{1s}	Inactive[a]	$\Delta K = \Delta K_i = 0$
2	C≡C stretch			
3	CH_3 deformation			
4	C-C stretch			
6	C-H stretch	A_{4s}	$\Delta K = \Delta K_i = 0$	Inactive[a]
7	CH_3 deformation			
8	C-C stretch			
9	C-H stretch	E_{1d}	$\Delta K = \pm 1$, $\Delta K_i = 0$	Inactive[a]
10	CH_3 deformation			
11	CH_3 rock			
12	Skeletal bend			
13	C-H stretch	E_{2d}	Inactive[a]	$\Delta K = \pm 1$, $\Delta K_i = 0$
14	CH_3 deformation			
15	CH_3 rock			
16	Skeletal bend			

[a] Neglecting the very weak transitions with ΔK or ΔK_i larger than 1.

TABLE 36

The Species of the Torsional and Rotational Wavefunctions of a Free-Rotor Ethylene Molecule in the Double Group $G_{16}^{\dagger}$ of Table A10. $K = |k_a + k_b|$ and $K_i = |k_a - k_b|$

K		Γ_{rot}	K_i	Γ_{tor}
0	J even	A_1^+	0	A_1^+
	J odd	B_1^-		
2n ± 1		E_{2d}	2n ± 1	E_{4d}
4n ± 2		$A_2^- + B_2^+$	4n ± 2	$B_2^+ + B_2^-$
4n		$A_1^+ + B_1^-$	4n	$A_1^+ + A_1^-$

TABLE 37

The Species of the Rotational (K_c) and Torsional (K_i) Wavefunctions of a CH_3NO_2 Type of Molecule in the Group G_{12} of Table A11

K_c		Γ_{rot}	K_i	Γ_{tor}
0	J even	A_1'	0	A_1'
	J odd	A_1''		
2n ± 1		$A_2' + A_2''$	6n ± 1	E''
2n		$A_1' + A_1''$	6n ± 2	E'
			6n ± 3	$A_1'' + A_2''$
			6n	$A_1' + A_2'$

TABLE A1

The Character Table of the $D_{\infty h}(M)$ Group

$D_{\infty h}(M)$	E	(12)	E*	(12)*
+s	1	1	1	1
-s	1	1	-1	-1
+a	1	-1	1	-1
-a	1	-1	-1	1

TABLE A2

The Character Table of the C_{2v} and $C_{2v}(M)$ Groups for H_2O

$C_{2v}(M)$ C_{2v}	E E	(12) C_2	E* $\sigma(ab)$	(12)* $\sigma(cb)$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	-1	1
B_2	1	-1	1	-1

TABLE A3

The Character Table of the Groups $C_{3v}(M)$ and C_{3v}

$C_{3v}(M)$	E	(123) (132)	(12)* (23)* (31)*
C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

TABLE A4

The Character Table of the Extended Molecular Symmetry Group $D_{\infty h}(EM)$. For Carbon Dioxide (p) = (12). This Table Could be more Compactly Written in four Columns Headed by E_ε, E^*_ε, $(p)^*_\varepsilon$, and $(p)_\varepsilon$

$D_{\infty h}(EM)$		E_0	E_ε	...	∞E^*_ε	$(p)^*_\pi$	$(p)^*_\varepsilon$	...	$\infty(p)_\varepsilon$
(+s)	Σ_g^+	1	1	...	1	1	1	...	1
(-a)	Σ_g^-	1	1	...	-1	1	1	...	-1
(+a)	Σ_u^+	1	1	...	1	-1	-1	...	-1
(-s)	Σ_u^-	1	1	...	-1	-1	-1	...	1
	Π_g	2	$2\cos\varepsilon$	...	0	2	$-2\cos\varepsilon$	...	0
	Π_u	2	$2\cos\varepsilon$	...	0	-2	$2\cos\varepsilon$	...	0
	Δ_g	2	$2\cos 2\varepsilon$	...	0	2	$-2\cos 2\varepsilon$	...	0
	Δ_u	2	$2\cos 2\varepsilon$	...	0	-2	$2\cos 2\varepsilon$	...	0
	...	...	...	...	...	...	...	...	...

TABLE A5

The Character Table for the Groups $C_s(M)$ and C_s

$C_s(M)$	E	E*
C_s	E	σ
A'	1	1
A"	1	-1

TABLE A6

The Character Table of the Group $D_{3h}(M)$ and of the Point Group D_{3h}. States of Positive Parity Transform According to Single Primed Representations, and States of Negative Parity Transform According to Double Primed Representations

$D_{3h}(M)$	E	(123) (132)	(12) (23) (31)	E*	(123)* (132)*	(12)* (23)* (31)*
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
A_2'	1	1	-1	1	1	-1
E'	2	-1	0	2	-1	0
A_1''	1	1	1	-1	-1	-1
A_2''	1	1	-1	-1	-1	+1
E''	2	-1	0	-2	+1	0

TABLE A7

The $C_s(M)$ Group of Rigid Staggered Methanol with the OH Group between the Atoms H_1 and H_2 of the CH_3 Group

$C_s(M)$	E	(12)*
A'	1	1
A''	1	-1

TABLE A8

The Character Table of the MS Group G_{36}

	E	(123)(456) (132)(465)	(14)(26)(35)(ab)(cd)* (15)(24)(36)(ab)(cd)* (16)(25)(34)(ab)(cd)*	(123)(465) (132)(456)	(132) (123) (456) (465)	(142635)(ab)(cd)* (143526)(ab)(cd)* (152436)(ab)(cd)* (153624)(ab)(cd)* (162534)(ab)(cd)* (163425)(ab)(cd)*
A_1	1	1	1	1	1	1
A_2	1	1	1	1	1	1
A_3	1	1	-1	1	1	-1
A_4	1	1	-1	1	1	-1
E_1	2	2	2	-1	-1	-1
E_2	2	2	-2	-1	-1	1
E_3	2	-1	0	2	-1	0
E_4	2	-1	0	2	-1	0
G	4	-2	0	-2	1	0

TABLE A8 (Continued)

(14)(25)(36)(ab)(cd) (15)(26)(34)(ab)(cd) (16)(24)(35)(ab)(cd)	(142536)(ab)(cd) (143625)(ab)(cd) (152634)(ab)(cd) (153426)(ab)(cd) (162435)(ab)(cd) (163524)(ab)(cd)	(12)(45)* (12)(56)* (12)(64)* (23)(45)* (23)(56)* (23)(64)* (13)(45)* (13)(56)* (13)(64)*
1	1	1
-1	-1	-1
1	1	-1
-1	-1	1
0	0	0
0	0	0
2	-1	0
-2	1	0
0	0	0

TABLE A9

The Character Table of the Group $C_{2v}(M)$ for a Rigid Acetone Molecule in the Conformation of Fig. 24

$C_{2v}(M)$	E	(14)(25)(36)(ab)	(23)(56)*	(14)(26)(35)(ab)*
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	-1	1
B_2	1	-1	1	-1

TABLE A10

The Character Table of the Extended Molecular Symmetry Group $G_{16}^{\dagger}$ for a Freely Rotating Ethylene-like Molecule

	E	A^3	D	A^2BD	AB	A^2E^*	A^3E^*	D^*	A^2BD	A^3B^*	A^2	A^2D	A^3B	A^2D^*
	1	4	2	4	1	2	4	2	4	1	1	2	1	2
A_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
B_1^+	1	1	-1	-1	1	1	1	-1	-1	1	1	-1	1	-1
B_2^+	1	-1	1	-1	1	1	-1	1	-1	1	1	1	1	1
E_s^+	2	0	0	0	-2	2	0	0	0	-2	2	0	-2	0
A_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
B_1^-	1	1	-1	-1	1	-1	-1	1	1	-1	1	-1	1	1
B_2^-	1	-1	1	-1	1	-1	1	-1	1	-1	1	1	1	-1
E_s^-	2	0	0	0	-2	-2	0	0	0	2	2	0	-2	0

(Continued)

TABLE A10 (Continued)

	E	A^3	D	A^2BD	AB	A^2E^*	A^3E^*	D*	A^2BD	A^3B^*	A^2	A^2D	A^3B	A^2D^*
	1	4	2	4	1	2	4	2	4	1	1	2	1	2
E_{1d}	2	0	0	0	-2	0	0	2	0	0	-2	0	2	-2
E_{2d}	2	0	0	0	-2	0	0	-2	0	0	-2	0	2	2
E_{3d}	2	0	-2	0	2	0	0	0	0	0	-2	2	-2	0
E_{4d}	2	0	2	0	2	0	0	0	0	0	-2	-2	-2	0

TABLE A11

The Character Table of the MS Group G_{12} for a Nitromethanelike Molecule, where 1, 2, 3 Number the Methyl Protons

	E	(123) (132)	(23)* (31)* (12)*	(45)	(123)(45) (132)(45)	(23)(45)* (31)(45)* (12)(45)*
A_1'	1	1	1	1	1	1
A_2'	1	1	-1	1	1	-1
E'	2	-1	0	2	-1	0
A_1''	1	1	1	-1	-1	-1
A_2''	1	1	-1	-1	-1	1
E''	2	-1	0	-2	1	0

TABLE A12

The Character Table of the MS Group G_{64} for a Torsionally Tunneling $Y_4X\text{-}XY_4$ Molecule. The Classes are Given in Table A13.

	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}
A_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
A_3	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
A_5	1	-1	1	1	1	1	-1	1	-1	1	1	-1	1	1	-1	1
A_6	1	-1	1	1	1	1	-1	1	-1	1	-1	1	-1	-1	1	-1
A_7	1	-1	1	1	1	1	-1	-1	1	-1	1	-1	1	-1	1	-1
A_8	1	-1	1	1	1	1	-1	-1	1	-1	-1	1	-1	1	-1	1
E_1	2	0	2	2	-2	-2	0	0	0	0	2	0	-2	0	0	0
E_2	2	0	2	2	-2	-2	0	0	0	0	-2	0	2	0	0	0
E_3	2	0	-2	2	2	-2	0	0	0	0	0	0	0	2	0	-2
E_4	2	0	-2	2	2	-2	0	0	0	0	0	0	0	-2	0	2
E_5	2	0	-2	2	-2	2	0	2	0	-2	0	0	0	0	0	0
E_6	2	0	-2	2	-2	2	0	-2	0	2	0	0	0	0	0	0
G_1	4	2	0	-4	0	0	-2	0	0	0	0	0	0	0	0	0
G_2	4	-2	0	-4	0	0	2	0	0	0	0	0	0	0	0	0

TABLE A13

The Classes of the MS Group G_{64}.

The Character Table is Given in Table A12

C_1	C_2	C_3	C_4	C_5	C_6
E	(1234) (1432) (5678) (5876)	(13)(24) (57)(68)	(13)(24)(57)(68)	(1234)(5678) (1432)(5876)	(1432)(5678) (1234)(5876)

C_7	C_8	C_9	C_{10}
(1432)(57)(68) (1234)(57)(68) (13)(24)(5678) (13)(24)(5876)	(15)(26)(37)(48) (16)(27)(38)(45) (17)(28)(35)(46) (18)(25)(36)(47)	(15263748) (16273845) (17283546) (18253647) (15483726) (16453827) (17463528) (18473625)	(1537)(2648) (1638)(2745) (1735)(2846) (1836)(2547)

C_{11}	C_{12}	C_{13}	C_{14}
(12)(34)(56)(78)* (14)(23)(56)(78)* (12)(34)(67)(85)* (14)(23)(67)(85)*	(13)(56)(78)* (24)(56)(78)* (13)(58)(67)* (24)(58)(67)* (12)(34)(57)* (12)(34)(68)* (14)(23)(57)* (14)(23)(68)*	(13)(57)* (13)(68)* (24)(57)* (24)(68)*	(15)(28)(37)(46)* (16)(25)(38)(47)* (17)(26)(35)(48)* (18)(27)(36)(45)*

C_{15}	C_{16}
(15283746)* (16253847)* (17263548)* (18273645)* (15463728)* (16473825)* (17483526)* (18453627)*	(1537)(2846)* (1638)(2547)* (1735)(2648)* (1836)(2745)*

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