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NOTES

$G_{162}$ : Molecular Symmetry Group for *t*-Butane and Other Three Equivalent Methyl Molecules

In his classic paper on the molecular symmetry group, Longuet-Higgins (1) gave the molecular symmetry group,  $G_{324}$ , for  $B(CH_3)_3$ , including internal rotation of the methyl groups as "feasible." However, the molecular symmetry group for *t*-butane and other  $C_{3v}$  three methyl molecules has not been published. In our recent work (2) on the  $\nu_1$  and  $2\nu_1$  spectra of  $(CH_3)_3C-C=CH$  we found it necessary to work out the details of this group in order to predict the possible splittings that could be introduced by lifting the 27-fold torsional quasidegeneracy of the ground state. Since this proved to be more than a trivial exercise, we are presenting the results in the hope that they may prove useful to other spectroscopists. In particular, a satisfactory analysis of the microwave spectrum of these molecules has not been published and symmetry considerations could be very helpful in this regard. Microwave studies of the excited torsional states of these molecules would be interesting since the top-top interactions would lead to "frustration"—it is not possible to coordinate rotation of the tops in such a way as to avoid unfavorable interactions.

The point group for these molecules is  $C_{3v}$ . In addition to the point group operations, the set of feasible operations should include the 27 operations that involve  $2\pi/3$  rotation of the three methyl tops. Adopting the notation of Stone (3), we label these methyl rotations  $\alpha = (1, 2, 3)$ ,  $\beta = (4, 5, 6)$ ,  $\gamma = (7, 8, 9)$  for clockwise rotation of the methyl carbons  $a, b, c$ . Let  $D = (a, b, c) (1, 4, 7) (2, 4, 8) (3, 6, 9)$  be the  $2\pi/3$  rotation about the  $C_{3v}$  symmetry axis of the molecule, and  $R = (b, c) (2, 3) (4, 7) (5, 9) (6, 8)^*$  be the reflection-inversion operation in one of the three  $\sigma_v$  planes. The group generated from these operations has 162 elements arranged in 13 classes. Table I gives the character table for this group. Since the number of classes is prime, the group cannot be factored into any smaller subgroups. The group has two pairs of separably degenerate, three-dimensional representations,  $(I_{4a}, I_{4b})$  and  $(I_{5a}, I_{5b})$ , respectively. Table II gives the multiplication table for the group. The correlation of the symmetry species to  $C_{3v}$  is given by  $A_1 \rightarrow A_1$ ;  $A_2 \rightarrow A_2$ ;  $E_1, E_3, E_4 \rightarrow E$ ;  $E_2 \rightarrow A_1 + A_2$ ;  $I_1, I_2, I_3 \rightarrow A_1 + A_2 + 2E$ ;  $I_4 \rightarrow 2A_1 + 2E$ ;  $I_5 \rightarrow 2A_2 + 2E$ .

TABLE I  
 Character Table for  $G_{162}$

	E	$\alpha\beta\gamma$	$\alpha\beta^{-1}$	$\alpha^{-1}\beta$	$\alpha$	$\alpha\beta$	$\alpha^{-1}\beta\gamma$	D	$\alpha D$	$\alpha^{-1}D$	R	$\beta R$	$\beta^{-1}R$	
	1	2	3	3	6	6	6	18	18	18	27	27	27	
$A_1$	1	1	1	1	1	1	1	1	1	1	1	1	1	$T_x(\text{even})$
$A_2$	1	1	1	1	1	1	1	1	1	1	-1	-1	-1	$R_x(\text{odd})$
$E_1$	2	2	2	2	2	2	2	-1	-1	-1	0	0	0	$(T_x, T_y) (R_x, R_y)$
$E_2$	2	2	2	2	-1	-1	-1	2	-1	-1	0	0	0	
$E_3$	2	2	2	2	-1	-1	-1	-1	2	-1	0	0	0	
$E_4$	2	2	2	2	-1	-1	-1	-1	-1	2	0	0	0	
$I_1$	6	-3	0	0	0	-3	3	0	0	0	0	0	0	
$I_2$	6	-3	0	0	3	0	-3	0	0	0	0	0	0	
$I_3$	6	-3	0	0	-3	3	0	0	0	0	0	0	0	
$I_{4a}$	3	3	$3e^*$	$3e$	0	0	0	0	0	0	1	$e$	$e^*$	
$I_{4b}$	3	3	$3e$	$3e^*$	0	0	0	0	0	0	1	$e^*$	$e$	
$I_{5a}$	3	3	$3e^*$	$3e$	0	0	0	0	0	0	-1	$-e$	$-e^*$	
$I_{5b}$	3	3	$3e$	$3e^*$	0	0	0	0	0	0	-1	$-e^*$	$-e$	

$e = \exp(2\pi i/3)$   
 $\alpha=(1,2,3); \beta=(4,5,6); \gamma=(7,8,9); D=(a,b,c)(1,4,7)(2,4,8)(3,6,9); R=(b,c)(2,3)(4,7)(5,9)(6,8)^*$

TABLE II  
 Product Table for  $G_{162}$ 

	$A_2$	$E_1$	$E_2$	$E_3$	$E_4$	$I_1$	$I_2$	$I_3$	$I_4$	$I_5$
$A_2$	$A_1$									
$E_1$	$E_1$	$A_1+A_2+E_1$								
$E_2$	$E_2$	$E_3+E_4$	$A_1+A_2+E_2$							
$E_3$	$E_3$	$E_2+E_4$	$E_1+E_4$	$A_1+A_2+E_3$						
$E_4$	$E_4$	$E_2+E_3$	$E_1+E_3$	$E_1+E_2$	$A_1+A_2+E_4$					
$I_1$	$I_1$	$2I_1$	$I_2+I_3$	$I_2+I_3$	$I_2+I_3$	$A_1+A_2+2E_1+I_1$ $+2I_3+I_4+I_5$				
$I_2$	$I_2$	$2I_2$	$I_1+I_3$	$I_1+I_3$	$I_1+I_3$	$E_2+E_3+E_4+2I_2$ $+I_3+I_4+I_5$	$A_1+A_2+2E_1+2I_1$ $+I_2+I_4+I_5$			
$I_3$	$I_3$	$2I_3$	$I_1+I_2$	$I_1+I_2$	$I_1+I_2$	$E_2+E_3+E_4+2I_1$ $+I_2+I_4+I_5$	$E_2+E_3+E_4+I_1$ $+2I_3+I_4+I_5$	$A_1+A_2+2E_1+2I_2$ $+I_3+I_4+I_5$		
$I_4$	$I_5$	$I_4+I_5$	$I_4+I_5$	$I_4+I_5$	$I_4+I_5$	$2I_1+2I_2+2I_3$	$2I_1+2I_2+2I_3$	$2I_1+2I_2+2I_3$	$2A_1+2E_1+2E_2+2E_3$ $+2E_4+2I_4+I_5$	
$I_5$	$I_4$	$I_4+I_5$	$I_4+I_5$	$I_4+I_5$	$I_4+I_5$	$2I_1+2I_2+2I_3$	$2I_1+2I_2+2I_3$	$2I_1+2I_2+2I_3$	$2A_2+2E_1+2E_2+2E_3$ $+2E_4+I_4+2I_5$	$2A_1+2E_1+2E_2+2E_3$ $+2E_4+2I_4+I_5$

An interesting feature of this group is that all the feasible operations are even permutations, thus the same representations  $A_1$  (even parity) and  $A_2$  (odd parity) apply to both Bosons and Fermions on the methyl groups. If we consider the common case of  $H$  or  $D$  on the methyl groups, we predict that there should be 512 or 19 683 spin functions, respectively. The representations spanned by these functions are given by

$$\Gamma_{\text{spin}}(H) = 20A_1 + 4A_2 + 20E_1 + 4E_2 + 2E_3 + 2E_4 + 16I_1 + 32I_2 + 8I_3 + 12I_4 + 4I_5$$

$$\Gamma_{\text{spin}}(D) = 275A_1 + 176A_2 + 440E_1 + 176E_2 + 168E_3 + 168E_4 + 704I_1$$

$$+ 968I_2 + 512I_3 + 388I_4 + 316I_5.$$

The vibrations of the  $(\text{CH}_3)_3X$ -group span the following irreducible representations: C-X stretch ( $A_1 + E_1$ ), C-X bend ( $A_1 + 2E_1$ ),  $\text{CH}_3$  s-stretch ( $A_1 + E_1$ ),  $\text{CH}_3$  a-stretch ( $I_2$ ),  $\text{CH}_3$  bend ( $A_1 + E_1 + 2I_2$ ), and  $\text{CH}_3$  torsion ( $A_2 + E_1$ ).

 TABLE III  
 Nuclear Spin Weights for Torsional Levels of Hydrogen Species

$ M_a M_b M_c\rangle$	$\Gamma_{\text{torsional}}$	K=0		K=3n±1	K=3n
		J=even	J=odd		
$ 0, 0, 0\rangle$	$A_1$	$A_1$ (20)	$A_2$ (4)	$E_1$ (20)	$A_1+A_2$ (20+4)
$ \pm 1, 0, 0\rangle$	$I_2$	$I_2$ (32)	$I_2$ (32)	$2I_2$ (64)	$2I_2$ (64)
$ \pm 1, \pm 1, 0\rangle$	$I_1$	$I_1$ (16)	$I_1$ (16)	$2I_1$ (32)	$2I_1$ (32)
$ \pm 1, \pm 1, 0\rangle$	$I_2$	$I_4$ (12)	$I_5$ (4)	$I_4+I_5$ (12+4)	$I_4+I_5$ (12+4)
$ \pm 1, \pm 1, \pm 1\rangle$	$I_3$	$I_3$ (8)	$I_3$ (8)	$2I_3$ (16)	$2I_3$ (16)
$ \pm 1, \pm 1, \pm 1\rangle$	$E_2$	$E_2$ (4)	$E_2$ (4)	$E_2+E_4$ (2+2)	$2E_2$ (8)

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In the high barrier limit, the ground vibrational state will be made 27-fold degenerate. Table III contains the nuclear spin weights for different  $J$  and  $K$  values for the torsional states that make up this degeneracy. We label the torsional states by their  $m$  quantum numbers of each top  $|m_a, m_b, m_c\rangle$  in the low barrier limit. Since the small-amplitude intramolecular vibrations have symmetry  $A_1, A_2,$  and  $E_1$ , the same as the rotational functions for  $0_0, 1_0,$  and  $1_1$ , respectively, we can, from the results given in Table III, calculate the spin weights for any excited vibrational state as well.

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representations: C-X stretch ( $A_1 + E_1$ ),  
CH<sub>3</sub> bend ( $A_1 + E_1 + 2I_2$ ), and CH<sub>3</sub>

## Hydrogen Species

$K=3n$
$A_1+A_2$ (20+4)
$2I_2$ (64)
$2I_1$ (32)
$I_4+I_5$ (12+4)
$2I_3$ (16)
$2E_2$ (8)