Letters

Vibrational Analysis for C_{60} and Other Fullerenes

Nakamoto and McKinney *(1)* provided a symmetry analysis of the vibrational modes of C_{60} and other fullerenes. I would like to supplement their presentation with another approach, in widespread use, which records the number of atoms that are unmoved by each symmetry operation, yielding the reducible representation Γ_{uma} *(2)*. This is particularly easy to do for C_{60} because only the identity operation and the 15 symmetry planes leave atoms unmoved, 60 and 4, respectively, as is shown in Table 1 of the Supplementary Materials.[W]

Multiplication of Γ_{uma} by the representation for translation in the *x, y,* and *z* directions (T_{1u} in I_h symmetry) yields, Γ_{tot}, the reducible representation for the 180 degrees of freedom of the C_{60} molecule. Γ_{tot} is then decomposed into the equivalent linear combination of I_h irreducible representations by the usual method as shown in Table 1 of the Supplementary Materials.[W] The symmetry of the vibrational modes is found by subtracting Γ_{trans} and Γ_{rot} from Γ_{tot}.

$$\Gamma_{vib} = 2A_g + 3T_{1g} + 4T_{2g} + 6G_g + 8H_g + A_u + 4T_{1u} + 5T_{2u} + 6G_u + 7H_u$$

IR-active modes have the same symmetry as *x, y,* and *z*. Raman active modes have the symmetry of the quadratic forms, x^2, *xy,* etc. Thus, we find four IR-active modes and ten Raman-active modes in agreement with experimental spectroscopic evidence *(1)*. The symmetry of the stretching modes can be determined by examining the behavior of the carbon–carbon bonds, Γ_{bonds}, under the symmetry operations of the I_h group. In addition, the symmetry of the π-electron density can be easily studied because $\Gamma_\pi = \Gamma_{uma}$. The combination of knowing the irreducible representations contributing to Γ_{vib} and Γ_π allows one to do an in-depth analysis of electronic spectrum of C_{60} utilizing the mechanism of vibronic coupling *(3)*.

It has been shown that this method of recording the number of unmoved atoms is ideally suited for computer programming environments that have matrix and vector algebra capability *(4)*. It is easy, for example, to prepare a Mathcad worksheet for any finite point group, which can then serve as a template for any molecule with that symmetry. The only thing that changes from one molecule to another within the same point group is the vector representing Γ_{uma}.

[W]Supplemental Material

A table synopsizing the values obtained for I_h irreducible representations of C_{60} is available in this issue of *JCE Online*.

Literature Cited

1. Nakamoto, K.; McKinney, M. A. *J. Chem. Educ.* **2000,** *77,* 775.
2. Harris, D. C.; Bertolucci, M. D. *Symmetry and Spectroscopy: An Introduction to Vibrational and Electronic Spectroscopy;* Dover Publications, Inc.: New York, 1989; p 141.
3. Leach, S.; Vervloet, M.; Despres, A.; Breheret, E.; Hare, J. P.; Dennis, T. J.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *Chem. Phys.* **1992,** *160,* 451–456.
4. Rioux, F. *J. Chem. Educ. Soft.* **1998**, Issue 9801MW.

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Table 1. Character Table for the Icosahedral Point Group

I_h	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$	i	$12S_{10}$	$12S_{10}^2$	$20S_6$	15σ	h =120
A_g	1	1	1	1	1	1	1	1	1	1	$x^2+y^2+z^2$
T_{1g}	3	1.618	-0.618	0	-1	3	1.618	-0.618	0	-1	R_x,R_y,R_z
T_{2g}	3	-0.618	1.618	0	-1	3	-0.618	1.618	0	-1	
G_g	4	-1	-1	1	0	4	-1	-1	1	0	
H_g	5	0	0	-1	1	5	0	0	-1	1	xy,xz,yz
A_u	1	1	1	1	1	-1	-1	-1	-1	-1	
T_{1u}	3	1.618	-0.618	0	-1	-3	-1.618	0.618	0	1	x, y, z
T_{2u}	3	-0.618	1.618	0	-1	-3	0.618	-1.618	0	1	
G_u	4	-1	-1	1	0	-4	1	1	-1	0	
H_u	5	0	0	-1	1	-5	0	0	1	-1	
Γ_{uma}	60	0	0	0	0	0	0	0	0	4	
$\Gamma_{tot}=\Gamma_{uma}\cdot T_{1u}$	180	0	0	0	0	0	0	0	0	4	
$\Gamma_{tot}\cdot A_g$	180	0	0	0	0	0	0	0	0	60	÷ h = 2
$\Gamma_{tot}\cdot T_{1g}$	540	0	0	0	0	0	0	0	0	-60	÷ h = 4
$\Gamma_{tot}\cdot T_{2g}$	540	0	0	0	0	0	0	0	0	-60	÷ h = 4
$\Gamma_{tot}\cdot G_g$	720	0	0	0	0	0	0	0	0	0	÷ h = 6
$\Gamma_{tot}\cdot H_g$	900	0	0	0	0	0	0	0	0	60	÷ h = 8
$\Gamma_{tot}\cdot A_u$	180	0	0	0	0	0	0	0	0	-60	÷ h = 1
$\Gamma_{tot}\cdot T_{1u}$	540	0	0	0	0	0	0	0	0	60	÷ h = 5
$\Gamma_{tot}\cdot T_{2u}$	540	0	0	0	0	0	0	0	0	60	÷ h = 5
$\Gamma_{tot}\cdot G_u$	720	0	0	0	0	0	0	0	0	0	÷ h = 6
$\Gamma_{tot}\cdot H_u$	900	0	0	0	0	0	0	0	0	-60	÷ h = 7

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Multiplication of Γ_{uma} by the representation for translation in the *x*, *y*, and *z* directions (T_{1u} in I_h symmetry) yields, Γ_{tot}, the reducible representation for the 180 degrees of freedom of the C_{60} molecule. Γ_{tot} is then decomposed into the equivalent linear combination of I_h irreducible representations by the usual method as shown in Table 1.

Table 1. Character Table for the Icosahedral Point Group

I_h	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$	i	$12S_{10}$	$12S_{10}^2$	$20S_6$	15σ	h =120
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T_{2g}	3	-0.618	1.618	0	-1	3	-0.618	1.618	0	-1	
G_g	4	-1	-1	1	0	4	-1	-1	1	0	
H_g	5	0	0	-1	1	5	0	0	-1	1	xy,xz,yz
A_u	1	1	1	1	1	-1	-1	-1	-1	-1	
T_{1u}	3	1.618	-0.618	0	-1	-3	-1.618	0.618	0	1	x, y, z
T_{2u}	3	-0.618	1.618	0	-1	-3	0.618	-1.618	0	1	
G_u	4	-1	-1	1	0	-4	1	1	-1	0	
H_u	5	0	0	-1	1	-5	0	0	1	-1	
Γ_{uma}	60	0	0	0	0	0	0	0	0	4	
$\Gamma_{tot}=\Gamma_{uma}\bullet T_{1u}$	180	0	0	0	0	0	0	0	0	4	
$\Gamma_{tot}\bullet A_g$	180	0	0	0	0	0	0	0	0	60	÷ h = 2
$\Gamma_{tot}\bullet T_{1g}$	540	0	0	0	0	0	0	0	0	-60	÷ h = 4
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$\Gamma_{tot}\bullet G_g$	720	0	0	0	0	0	0	0	0	0	÷ h = 6
$\Gamma_{tot}\bullet H_g$	900	0	0	0	0	0	0	0	0	60	÷ h = 8
$\Gamma_{tot}\bullet A_u$	180	0	0	0	0	0	0	0	0	-60	÷ h = 1
$\Gamma_{tot}\bullet T_{1u}$	540	0	0	0	0	0	0	0	0	60	÷ h = 5
$\Gamma_{tot}\bullet T_{2u}$	540	0	0	0	0	0	0	0	0	60	÷ h = 5
$\Gamma_{tot}\bullet G_u$	720	0	0	0	0	0	0	0	0	0	÷ h = 6
Γ_{tot}ßH$_u$	900	0	0	0	0	0	0	0	0	-60	â h = 7

$\Gamma_{tot} = 2A_g + 4T_{1g} + 4T_{2g} + 6G_g + 8H_g + A_u + 5T_{1u} + 5T_{2u} + 6G_u + 7H_u$