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## The numbers of anharmonic potential constants of the fullerenes C<sub>60</sub> and C<sub>70</sub>

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**Abstract.** The number of independent potential constants of degree  $n$  of a molecule is obtained from the reduction of the symmetric  $n$ th power of the representation  $\Gamma_{\text{vib}}$  of the vibrational degrees of freedom in the point group of the molecule. As an illustration, this theory is applied to the cubic and quartic potentials of the fullerenes C<sub>60</sub> (point group I<sub>h</sub>) and C<sub>70</sub> (point group D<sub>5h</sub>). The numbers are extremely large, indicating that models with a considerably reduced number of parameters will be required for practical calculations.

### 1. Introduction

Ever since the discovery (Kroto *et al* 1985, Krätschmer *et al* 1990) of the geodesic carbon clusters—the fullerenes—there has been great interest in their vibrational properties. The best-known clusters C<sub>60</sub> and C<sub>70</sub> belong to point groups with five-fold axes, the icosahedral I<sub>h</sub> group for C<sub>60</sub> and the dihedral group D<sub>5h</sub> for C<sub>70</sub>. With  $N = 60$  atoms, C<sub>60</sub> has  $3N - 6 = 174$  internal degrees of freedom with 46 distinct vibrational frequencies, the vibrational coordinates having the representation

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

whereas C<sub>70</sub> has 204 internal degrees of freedom with 122 distinct frequencies, and coordinates transforming as

$$\Gamma_{\text{vib}} = 12A'_1 + 9A''_1 + 9A'_2 + 10A''_2 + 21E'_1 + 19E''_1 + 22E'_2 + 20E''_2. \quad (2)$$

A group-theoretical method of calculating the number of distinct frequencies was published by Watson (1992). The numbers of infrared-active modes are 4 (T<sub>1u</sub>) for C<sub>60</sub> and 31 (E', A''<sub>2</sub>) for C<sub>70</sub>, while the numbers of Raman-active modes are 10 (A<sub>g</sub>, H<sub>g</sub>) for C<sub>60</sub> and 53 (A'<sub>1</sub>, E'<sub>2</sub>, E''<sub>1</sub>) for C<sub>70</sub>. Both molecules show a mutual exclusion rule between infrared- and Raman-active modes. For C<sub>60</sub> this is the usual consequence of a centre of symmetry, whereas for C<sub>70</sub> the exclusion does not appear to be associated with any particular symmetry operation.

There are several harmonic vibrational analyses for C<sub>60</sub> and C<sub>70</sub> in the literature (see, for example, Onida and Benedek 1992, Onida *et al* 1994), but we are not aware of any discussion of the anharmonic potential constants. Although the smallness of the temperature dependence of the positions and shapes of the gas-phase infrared emission bands of C<sub>60</sub> and C<sub>70</sub> (Nemes *et al* 1994) suggests that the vibrational potential function for these fullerenes

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is essentially harmonic, it is nevertheless important to know more about their vibrational anharmonicities. In this paper we examine the numbers of the leading anharmonic potential constants (cubic and quartic) for these molecules. These numbers are of interest in their own right, and will require to be known in any future anharmonic vibrational analyses, and in studies of the effects of vibrational resonances due to cubic and quartic potential constants. The cubic anharmonic constants also contribute to the dependence of the rotational constants on vibrational quantum numbers, and will be relevant if it should eventually be possible to observe the rotational profiles of the bands in the vibrational spectrum.

## 2. Method

The number of potential constants of degree  $n$  is obtained from the reduction of the symmetric  $n$ th power of the representation  $\Gamma_{\text{vib}}$  of the vibrational degrees of freedom, as given in equation (1) or (2). The number of  $n$ th degree potential constants is the number of times that the totally symmetric representation of the point group appears in this reduction (Watson 1972).

The  $n$ th power of a representation of a group can be separated into different components according to the irreducible representations of the symmetric group  $S_n$ , the permutation group on  $n$  objects. Here we consider only the simplest components, the symmetric  $n$ th power and the antisymmetric  $n$ th power. The former arises in vibration-rotation spectroscopy in a number of contexts. For example, the set of states corresponding to the quantum number  $v$  of a degenerate vibrational mode belongs to the symmetric  $v$ th power of the irreducible representation of the mode (Wilson *et al* 1980, pp 151–5), and the number of independent centrifugal terms of degree  $n$  is the number of times the totally symmetric representation of the point group is contained in the symmetric  $n$ th power of the representation of the components of the angular momentum  $\mathbf{J}$  (Watson 1977, pp 11–2). Similarly, the exclusion principle for states of  $n$  equivalent bosons in degenerate spin-orbitals requires that they belong to the symmetric  $n$ th power of the representation of the spin-orbital, whereas for  $n$  equivalent fermions they belong to the antisymmetric  $n$ th power.

For vibration-rotation spectroscopists the most familiar discussion of the symmetric  $n$ th power is that of Wilson *et al* (1980, pp 151–5). For any operator  $R$  they consider diagonalizing the representation matrix in the base representation  $\Gamma$  to get the eigenvalues  $R_s$ ,  $s = 1, 2, \dots, d$ . Then the representation matrices for the symmetric and antisymmetric  $n$ th powers are also diagonal, and have characters

$$\chi_n^+(R) = h_n(R_1, R_2, \dots, R_d), \quad (3)$$

$$\chi_n^-(R) = a_n(R_1, R_2, \dots, R_d). \quad (4)$$

Here  $h_n(R_1, R_2, \dots, R_d)$  is the  $n$ th homogeneous product sum of the  $R_s$ ,

$$h_n(R_1, R_2, \dots, R_d) = \sum_{i,j,k,\dots=0}^n \delta_{i+j+k+\dots,n} R_1^i R_2^j R_3^k \dots, \quad (5)$$

and  $a_n(R_1, R_2, \dots, R_d)$  is the  $n$ th elementary symmetric function, linear in each  $R_s$ ,

$$a_n(R_1, R_2, \dots, R_d) = \sum_{i,j,k,\dots=0}^1 \delta_{i+j+k+\dots,n} R_1^i R_2^j R_3^k \dots \quad (6)$$

For  $n > d$ ,  $\chi_n^-(R)$  vanishes because the conditions on the indices  $i, j, \dots$  in equation (6) cannot be satisfied. Properties of the functions  $h_n(R_1, R_2, \dots, R_d)$  and  $a_n(R_1, R_2, \dots, R_d)$

and relations between them and the power sums

$$\chi(R^n) = S_n(R_1, R_2, \dots, R_d) = \sum_{s=1}^d R_s^n \quad (7)$$

are studied in the theory of symmetric functions (Littlewood 1958, ch V), usually applied to the roots of polynomial equations.

Wilson *et al* (1980, p 153) give recursion relations in  $n$  for the cases  $d = 2$  and  $3$ , and refer to Tisza (1933) for  $d = 4$  and  $5$ . For general  $d$ , Tisza (1933) and Watson (1972) give explicit character formulae for  $[\Gamma^n]$  up to  $n = 4$ , while Zhou and Pulay (1989) give the recursion relation

$$\chi_n^\pm(R) = \frac{1}{n} \sum_{m=1}^n (\pm 1)^{m-1} \chi(R^m) \chi_{n-m}^\pm(R). \quad (8)$$

This recursion relation can be solved (Littlewood 1958, ch V) to give an explicit formula in terms of an  $n \times n$  determinant

$$\chi_n^\pm(R) = \frac{1}{n!} \begin{vmatrix} \chi(R) & \mp 1 & & & & \\ \chi(R^2) & \chi(R) & \mp 2 & & & \\ \chi(R^3) & \chi(R^2) & \chi(R) & \mp 3 & & \\ \dots & \dots & \dots & \dots & \dots & \\ \dots & \dots & \dots & \dots & \dots & \mp(n-1) \\ \chi(R^n) & \chi(R^{n-1}) & \chi(R^{n-2}) & \dots & \dots & \chi(R) \end{vmatrix}, \quad (9)$$

where the blank elements are zero. This formula is readily shown to reduce to the specific cases for  $n = 2-6$  given by Tisza (1933), Watson (1972) and Zhou and Pulay (1989).

### 3. Results

The present calculation essentially consists of using the characters of  $\Gamma_{\text{vib}}$  for  $\text{C}_{60}$  or  $\text{C}_{70}$  from equation (1) or (2) in equation (9) for  $n = 3$  and  $n = 4$ . Although the algebraic task is, in principle, straightforward, the complexities are considerable, and so hand calculations are difficult and prone to errors. We have therefore written computer programs in Pascal to carry out the group-theoretical calculations, and the results below were obtained in this fashion.

**Table 1.** Characters of symmetric powers  $[\Gamma_{\text{vib}}^n]$  for  $\text{C}_{60}$ .

$I_h$	$E$	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$
$\Gamma_{\text{vib}}$	174	$-2\eta^+$	$-2\eta^-$	0	2
$[\Gamma_{\text{vib}}^2]$	15 225	$1 + 3\eta^+$	$1 + 3\eta^-$	0	89
$[\Gamma_{\text{vib}}^3]$	893 200	$-2(2 + \eta^+)$	$-2(2 + \eta^-)$	58	176
$[\Gamma_{\text{vib}}^4]$	39 524 100	$1 + 3\eta^+$	$1 + 3\eta^-$	0	4004
$I_h$	$i$	$12S_{10}$	$12S_{10}^3$	$20S_6$	$15\sigma$
$\Gamma_{\text{vib}}$	0	0	0	0	4
$[\Gamma_{\text{vib}}^2]$	87	$-\eta^+$	$-\eta^-$	0	95
$[\Gamma_{\text{vib}}^3]$	0	0	0	0	360
$[\Gamma_{\text{vib}}^4]$	3828	$\eta^+$	$\eta^-$	0	4540

$$\eta^\pm = (1 \pm \sqrt{5})/2, \eta^+ = 2 \cos \pi/5, \eta^- = 2 \cos 3\pi/5.$$

**Table 2.** Characters of symmetric powers  $[\Gamma_{\text{vib}}^n]$  for  $C_{70}$ .

$D_{5h}$	$E$	$2C_5$	$2C_5^2$	$5C_2$
$\Gamma_{\text{vib}}$	204	$-2\eta^+$	$-2\eta^-$	2
$[\Gamma_{\text{vib}}^2]$	20 910	$1 + 3\eta^+$	$1 + 3\eta^-$	104
$[\Gamma_{\text{vib}}^3]$	1 435 820	$-2(2 + \eta^+)$	$-2(2 + \eta^-)$	206
$[\Gamma_{\text{vib}}^4]$	74 303 685	$1 + 3\eta^+$	$1 + 3\eta^-$	5459
$D_{5h}$	$\sigma_h$	$2S_5$	$2S_5^3$	$5\sigma_v$
$\Gamma_{\text{vib}}$	10	0	0	4
$[\Gamma_{\text{vib}}^2]$	152	$-\eta^-$	$-\eta^+$	110
$[\Gamma_{\text{vib}}^3]$	1 190	0	0	420
$[\Gamma_{\text{vib}}^4]$	10 803	$\eta^-$	$\eta^+$	6085

$$\eta^\pm = (1 \pm \sqrt{5})/2, \eta^+ = 2 \cos \pi/5, \eta^- = 2 \cos 3\pi/5.$$

Tables 1 and 2 contain the characters of  $[\Gamma_{\text{vib}}^n]$  for  $n = 1-4$  for the two fullerenes in question. Upon reducing the symmetric power representations for  $C_{60}$  in table 1, we obtain the following structures:

$$[\Gamma_{\text{vib}}^2] = 151A_g + 126A_u + 361T_{1g} + 380T_{1u} + 359T_{2g} + 379T_{2u} + 510G_g + 504G_u + 661H_g + 630H_u \quad (10)$$

$$[\Gamma_{\text{vib}}^3] = 7519A_g + 7429A_u + 22\,262T_{1g} + 22\,352T_{1u} + 22\,263T_{2g} + 22\,353T_{2u} + 29\,784G_g + 29\,784G_u + 37\,274H_g + 37\,184H_u \quad (11)$$

$$[\Gamma_{\text{vib}}^4] = 330\,468A_g + 329\,269A_u + 987\,131T_{1g} + 988\,075T_{1u} + 987\,130T_{2g} + 988\,073T_{2u} + 1317\,597G_g + 1317\,342G_u + 1648\,065H_g + 1646\,611H_u. \quad (12)$$

Thus the numbers of independent second-, third- and fourth-degree potential constants of  $C_{60}$  are 151, 7519 and 330 468, respectively.

The analogous numbers for  $C_{70}$  in the  $D_{5h}$  point group are

$$[\Gamma_{\text{vib}}^2] = 1107A'_1 + 1037A''_1 + 1000A'_2 + 1040A''_2 + 2107E'_1 + 2076E''_1 + 2105E'_2 + 2075E''_2 \quad (13)$$

$$[\Gamma_{\text{vib}}^3] = 72\,006A'_1 + 71\,677A''_1 + 71\,693A'_2 + 71\,784A''_2 + 143\,701E'_1 + 143\,463E''_1 + 143\,702E'_2 + 143\,464E''_2 \quad (14)$$

$$[\Gamma_{\text{vib}}^4] = 3718\,611A'_1 + 3714\,488A''_1 + 3712\,839A'_2 + 3714\,801A''_2 + 7431\,449E'_1 + 7429\,289E''_1 + 7431\,448E'_2 + 7429\,287E''_2. \quad (15)$$

Therefore in  $C_{70}$  there are 1107 quadratic, 72 006 cubic and 3718 611 quartic potential constants.

These results can be examined in more detail, to find the complete symmetry classification of the constants in terms of the vibrational modes that they involve. The symmetry classification for the quadratic terms is obvious, because they only involve coordinates of the same symmetry species, but the cubic and quartic terms do involve cross terms and would require a considerable amount of space to present. Instead we only quote here a portion of these results, and only for the cubic potential constants.

As there are a great number of optically 'silent' modes—that is, modes that cannot be seen in infrared or Raman spectroscopy—in both  $C_{60}$  and  $C_{70}$  (32 for the former and 38 for the latter), anharmonic couplings among the various vibrational levels will generally connect infrared and/or Raman active and silent modes. Thus it may be of some value to

know those cubic terms in both fullerenes that couple optically active modes. Among the 62 types of non-vanishing terms in  $[\Gamma_{\text{vib}}^3]$  for  $C_{60}$  there are 39 types of ternary combinations of the  $I_h$  species that contain at least one optically active species, and their numbers are:

$$\begin{array}{llll}
 4A_g A_g A_g, & 240H_g H_g H_g, & 12A_g T_{1g} T_{1g}, & 20A_g T_{2g} T_{2g}, \\
 42A_g G_g G_g, & 72A_g H_g H_g, & 2A_g A_u A_u, & 20A_g T_{1u} T_{1u}, \\
 30A_g T_{2u} T_{2u}, & 42A_g G_u G_u, & 56A_g H_u H_u, & 48T_{1g} T_{1g} H_g, \\
 84T_{1g} H_g H_g, & 18T_{1g} T_{1u} T_{1u}, & 80T_{2g} T_{2g} H_g, & 112T_{2g} H_g H_g, \\
 168G_g G_g H_g, & 384G_g H_g H_g, & 80H_g T_{1u} T_{1u}, & 120H_g T_{2u} T_{2u}, \\
 168H_g G_u G_u, & 448H_g H_u H_u, & 96T_{1g} T_{2g} H_g, & 144T_{1g} G_g H_g, \\
 12T_{1g} A_u T_{1u}, & 84T_{1g} T_{1u} H_u, & 192T_{2g} G_g H_g, & 96T_{2g} T_{1u} G_u, \\
 112T_{2g} T_{1u} H_u, & 120G_g T_{1u} T_{2u}, & 144G_g T_{1u} G_u, & 168G_g T_{1u} H_u, \\
 56H_g A_u H_u, & 160H_g T_{1u} T_{2u}, & 192H_g T_{1u} G_u, & 224H_g T_{1u} H_u, \\
 240H_g T_{2u} G_u, & 280H_g T_{2u} H_u, & 672H_g G_u H_u, & 
 \end{array} \quad (16)$$

For  $C_{70}$ , 22 of the 23 non-vanishing types of terms in  $[\Gamma_{\text{vib}}^3]$  contain at least one infrared- or Raman-active species:

$$\begin{array}{llll}
 364A'_1 A'_1 A'_1, & 540A'_1 A'_2 A'_2, & 2772A'_1 E'_1 E'_1, & 3036A'_1 E'_2 E'_2, \\
 540A'_1 A'_1 A''_1, & 660A'_1 A'_2 A''_2, & 2280A'_1 E'_1 E''_1, & 2520A'_1 E'_2 E''_2, \\
 1890A'_2 E'_1 E'_1, & 2079A'_2 E'_2 E'_2, & 1539A'_2 E'_1 E''_1, & 5082E'_1 E'_1 E'_2, \\
 5313E'_1 E'_2 E'_2, & 4410E'_1 E'_2 E''_2, & 4180E'_2 E'_1 E''_1, & 810A'_2 A'_1 A'_2, \\
 3591E'_1 A'_1 E''_1, & 3990E'_1 A'_2 E''_1, & 7980E'_1 E'_1 E''_2, & 3960E'_2 A'_1 E''_2, \\
 4400E'_2 A'_2 E''_2, & 8360E'_2 E'_1 E''_2, & & 
 \end{array} \quad (17)$$

The numbers of non-vanishing types of quartic potential constants for  $C_{60}$  and  $C_{70}$  are 289 and 86, respectively, and their distribution among the various quaternary combinations of species is significantly more involved than for the cubic terms. Detailed results are available from LN on request.

#### 4. Conclusion

As might have been expected, the numbers of anharmonic potential constants of the fullerenes are extremely large, and any kind of detailed consideration of them would be prohibitively complicated. Progress in understanding anharmonic effects in these molecules will depend on the development of models, for example involving local interactions between valence coordinates, that depend on a limited number of parameters. The large number of potential constants allowed by symmetry will then be expressible as functions of this smaller number of parameters. Nevertheless, it is useful to know these numbers in order to ensure that all the terms allowed by symmetry are included in calculations.

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