

Symmetry for lattice modes in C_{60} and alkali-metal-doped C_{60}

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We present a group-theoretical analysis relevant to the interpretation of recent experimental observations of Raman-scattering spectroscopy in C_{60} and alkali-metal-doped C_{60} . The group-theoretical analysis makes use of two space groups, both of which reduce the icosahedral point-group symmetry of the isolated C_{60} molecule to the cubic group T_h . The space group for the fcc arrangement of fullerene is T_h^6 and corresponds to the low-temperature solid phase of pristine C_{60} . The bcc arrangement for solid M_6C_{60} , where M is an alkali metal, is consistent with the space group T_h^5 and is the symmetry considered for the fully doped alkali-metal material. The experimental Raman spectra show line splittings which are consistent with a symmetry lowering to T_h symmetry for the fullerene molecule. However, the polarization selection rules observed experimentally indicate a further lowering of the symmetry, beyond cubic symmetry.

I. INTRODUCTION

Interest in the phonon spectrum of C_{60} and C_{60} -derived materials has been aroused by the relatively high superconducting transition temperatures that have been recently reported: alkali-metal-doped K_xC_{60} ($T_c = 18$ K),^{1,2} Rb_xC_{60} ($T_c = 29$ K),³ Cs_xC_{60} ($T_c = 30$ K),⁴ and $Rb_xCs_yC_{60}$ ($T_c = 33$ K).⁵ In this paper we address the symmetry of pristine and doped C_{60} crystalline materials and how this symmetry affects the observed Raman spectra.

The room-temperature Raman spectra for both pristine C_{60} and alkali-metal-doped M_6C_{60} ($M = K, Rb, Cs$) are surprisingly simple,^{6,7} considering the large number of degrees of freedom within the unit cell. The spectra of the alkali-metal-doped M_6C_{60} compounds ($M = K, Rb, Cs$) show great similarities to one another and to pristine C_{60} . These observations indicate the importance of symmetry, and suggest that we can model the effect of the alkali-metal doping on the lattice modes of solid C_{60} in a similar manner to the approach taken in carrying out the lattice-dynamics studies in alkali-metal intercalated graphite.^{8,9} Both in C_{60} and in graphite intercalation compounds (GIC's), the alkali metal interacts only weakly with the near-neighbor carbon atoms, so that the main effect of intercalation on the lattice modes is the charge transfer associated with the alkali-metal intercalation process. This charge transfer modifies the force constants describing the C-atom motion, which in the case of donor dopants leads to a softening of the phonon mode frequencies in both the GIC's and C_{60} -based materials.

II. GROUP-THEORETICAL FRAMEWORK

A number of authors have discussed the vibrational spectra of molecules with icosahedral symmetry both experimentally^{1,6,10} and theoretically.¹¹⁻¹⁵ In the following we will consider first the highest-symmetry space group which is appropriate for C_{60} and M_xC_{60} , even though it is only for the low-temperature phase of C_{60} that the space group T_h^6 has been positively identified.^{16,17} In the fully doped material M_6C_{60} the space group T_h^5 or $Im\bar{3}$ has been identified experimentally.¹⁸ These two space groups either represent the actual structure of solid C_{60} and M_6C_{60} or represent a first approximation to the actual structure of the samples which have been studied optically.^{6,7,10}

A. Group theory for C_{60}

The character table for the full icosahedral group I_h which characterizes an isolated C_{60} molecule is shown in Table I. To calculate the symmetries of the vibrational modes (or of the electronic orbitals) one must know the symmetries associated with linear combinations of the atomic sites of the molecule or unit cell of the lattice. The site symmetry for an isolated C_{60} molecule is summarized in Table II, where the characters for the equivalence transformation of the atom sites $\chi^{a.s.}$ are given for various symmetric placements of atoms in positions of high symmetry within the I_h point group: X atoms (e.g., guest species) at the 12 vertices of the regular icosahedron, carbon atoms on the centers of the 20 hexagonal faces, the centers of the 30 edges, and at the 60 vertices of

TABLE I. Character table for the point group I_h , where $\tau = (1 + \sqrt{5})/2$. Note: C_5 and C_5^{-1} are in different classes, labeled $12C_5$ and $12C_5^2$ in the character table. Then $iC_5 = S_{10}^{-1}$ and $iC_5^{-1} = S_{10}$ are in the classes labeled $12S_{10}^3$ and $12S_{10}$, respectively. Also $iC_2 = \sigma_v$.

I_h	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$	i	$12S_{10}^3$	$12S_{10}$	$20S_3$	$15\sigma_v$	Basis functions
A_g	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	$x^2 + y^2 + z^2$
F_{1g}	+3	$+\tau$	$1-\tau$	0	-1	+3	τ	$1-\tau$	0	-1	(R_x, R_y, R_z)
F_{2g}	+3	$1-\tau$	$+\tau$	0	-1	+3	$1-\tau$	τ	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	$\begin{cases} 2z^2 - x^2 - y^2 \\ x^2 - y^2 \\ xy \\ xz \\ yz \end{cases}$
A_u	+1	+1	+1	+1	+1	-1	-1	-1	-1	-1	
F_{1u}	+3	$+\tau$	$1-\tau$	0	-1	-3	$-\tau$	$\tau-1$	0	+1	(x, y, z)
F_{2u}	+3	$1-\tau$	$+\tau$	0	-1	-3	$\tau-1$	$-\tau$	0	+1	(x^3, y^3, z^3)
G_u	+4	-1	-1	+1	0	-4	+1	+1	-1	0	$\begin{cases} x(z^2 - y^2) \\ y(x^2 - z^2) \\ z(y^2 - x^2) \\ xyz \end{cases}$
H_u	+5	0	0	-1	+1	-5	0	0	+1	-1	

TABLE II. Characters for the equivalence transformation $\chi^{a.s.}$ of various LCAO's in icosahedral I_h symmetry.

I_h	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$	i	$12S_{10}^3$	$12S_{10}$	$20S_3$	$15\sigma_v$	$\chi^{a.s.}$
X_{12}	12	2	2	0	0	0	0	0	0	4	$\Rightarrow A_g + H_g + F_{1u} + F_{2u}$
C_{20}	20	0	0	2	0	0	0	0	0	4	$\Rightarrow A_g + G_g + H_g + F_{1u} + F_{2u} + G_u$
C_{30}	30	0	0	0	2	0	0	0	0	4	$\Rightarrow A_g + G_g + 2H_g + F_{1u} + F_{2u} + G_u + H_u$
C_{60}	60	0	0	0	0	0	0	0	0	4	$\Rightarrow A_g + F_{1g} + F_{2g} + 2G_g + 3H_g + 2F_{1u} + 2F_{2u} + 2G_u + 2H_u$

TABLE III. Vibrational modes in molecules with icosahedral symmetry.

Molecule	A_g^a	F_{1g}	F_{2g}	G_g	H_g^b	A_u	F_{1u}^c	F_{2u}	G_u	H_u
X_{12}	1			1	2		1	1	1	1
X_{20}	1		1	2	3		1	2	2	2
X_{30}	1	1	2	3	4		2	3	3	3
C_{60}	2	3	4	6	8	1	4	5	6	7
C_{60} (radial)	1	1	1	2	3		2	2	2	2
C_{60} (tangential)	1	2	3	4	5	1	2	3	4	5
$X_{12}C_{60}$	3	4	4	7	10	1	6	6	7	8
$X_{12}C_{60}$ (radial)	2	1	1	2	4		3	3	2	2
$X_{12}C_{60}$ (tangential)	1	3	3	5	6	1	3	3	5	6

^a Raman-active mode is seen only in \parallel, \parallel polarization.

^b Raman-active mode is seen in both \parallel, \parallel and \parallel, \perp polarizations.

^c Infrared-active mode.

the regular truncated icosahedron. The irreducible representations of the point group I_h corresponding to each configuration are also listed in Table II. The I_h symmetry of the C₆₀ molecule is the highest possible point-group symmetry and is the starting point for all the applications of group theory in this paper.

For example, a hypothetical X_1C_{60} molecule, where the single X atom is placed in the center of the icosahedron, maintains I_h symmetry and $\chi^{a.s.}(X_1) = A_g$. A hypothetical $X_{12}C_{60}$ molecule, where the 12 X atoms are at the vertices of the regular icosahedron, also exhibits I_h symmetry. Following Table II, the equivalence transformation for the 12 X atoms in $X_{12}C_{60}$ yields the irreducible representations of the I_h point group

$$\chi^{a.s.}(X_{12}) = A_g + F_{1u} + F_{2u} + H_g,$$

which occur in addition to those for the 60 carbon atoms,

$$\chi^{a.s.}(C_{60}) = A_g + F_{1g} + F_{2g} + 2G_g + 3H_g \\ + 2F_{1u} + 2F_{2u} + 2G_u + 2H_u.$$

1. Vibrational modes

Although there are 180 degrees of freedom (3×60) for each C₆₀ molecule, the icosahedral symmetry gives rise to a number of degenerate modes, so that only 46 distinct mode frequencies are expected for the C₆₀ molecule.

The symmetries of the vibrational modes of a molecule with I_h symmetry are found by taking the direct product of $\chi^{a.s.}$ in Table III with the characters for a vector in I_h symmetry, which corresponds to the irreducible representation F_{1u} . The resulting symmetries for the normal modes of the icosahedral molecules are listed in Table III according to their symmetry types and multiplicities. The Raman-active modes have A_g and H_g symmetry and the infrared-active modes have F_{1u} symmetry. One can see from the basis functions listed in Table I that the symmetry of the Raman tensor allows \parallel, \parallel scattering for A_g modes, and both \parallel, \parallel and \parallel, \perp scattering for H_g modes. The remaining modes are silent unless some symmetry-lowering perturbation (e.g., the crystal field associated with the condensed phase) turns them on. Such symmetry-lowering perturbations would also modify the Raman-scattering selection rules. In the extreme case where the point-group symmetry is lowered to C_1 , there are $180 - 6 = 174$ vibrational modes and each mode is Raman active and would be seen in both the \parallel, \parallel and \parallel, \perp scattering geometries.

In listing the vibrational modes for the molecular units C₆₀ and $X_{12}C_{60}$ in Table III, the six degrees of freedom associated with the center of mass (translations and rotations) have been subtracted. The vibrational modes in the solid state arising from these subtracted molecular modes are treated specially in our discussion below for the lattice modes in the space group.

2. Electronic structure

Using the same $\chi^{a.s.}$ as are given in Table II, the symmetries of the electronic levels of the molecule can be

found by taking the direct product of $\chi^{a.s.}$ with A_g for s functions, with F_{1u} for p functions and with H_g for d functions. The symmetries of the various molecular orbitals for the icosahedral molecules are listed in Table IV (see Fowler and Woolrich¹⁹). For the C₆₀ molecule, the p functions are listed in terms of radial π orbitals and tangential σ orbitals. However, in any molecular orbital calculation, the radial and tangential orbitals with the same symmetry will hybridize. The entries in Table IV can be used to analyze spectral data showing, for example, electric-dipole selection rules between molecular levels.

B. Symmetry of solid C₆₀

It has recently been determined by x-ray diffraction¹⁶ that, below the ordering temperature of ~ 249 K, pristine C₆₀ crystallizes in a simple cubic structure with space group T_h^6 (Ref. 17) where there are four C₆₀ molecules (or 240 carbon atoms) per unit cell. The T_h point-group symmetry is shown in Table V along with the basis functions for these irreducible representations. The basis functions imply that the A_g , E_g , and T_g modes are Raman active with A_g and E_g mode scattering appearing only for the \parallel, \parallel geometry and T_g modes only for the \parallel, \perp geometry. The T_h^6 space-group symmetry can be maintained on doping provided the dopant is placed on the equivalent sites of the space group. These equivalent sites are enumerated in Table VI for T_h^6 symmetry and in Table VII for T_h^5 symmetry. The space group T_h^6 has been identified for the doped material for $x \leq 3$; T_h^6 is also the low-temperature phase for the undoped material, $x = 0$.^{16,17} However, the fully doped material K₆C₆₀ has been reported to show a bcc structure,²⁰ consistent with the bcc space group T_h^5 with T_h site symmetry for the two C₆₀ molecules per nonprimitive unit cell. We will therefore consider both the T_h^6 and T_h^5 structures in the present work.

Since the space groups T_h^6 and T_h^5 are probably the highest symmetries that can be found for C₆₀-related materials, it is useful to consider the T_h^6 and T_h^5 space groups as an approximate symmetry for the doped materials (T_h^6 for weakly doped and T_h^5 for nearly fully doped) and to consider the lower-symmetry space groups, when they are identified, as resulting from perturbations of these high-symmetry groups.

We therefore model the room-temperature structure of the solid single-crystal film of C₆₀ as a simple cubic lattice with four molecules per unit cell having T_h^6 space-group symmetry, where each molecule having molecular orbitals associated with the C₆₀ molecules is in a site with T_h symmetry (see Table V). The phonon-dispersion relations and the electronic structure for C₆₀ are then modeled in terms of weakly coupled, isotropically oriented, freely rotating (at high temperature) C₆₀ icosahedral molecules located at fcc T_h^6 site positions.

According to the site symmetries for space group T_h^6 shown in Table VI, the four C₆₀ molecules per unit cell are on a sites. A dopant atom (e.g., an alkali-metal atom) can be placed in a tetrahedral b site giving the stoichiometry M_1C_{60} , or in an octahedral c site giving the

TABLE IV. Molecular orbitals in molecules with icosahedral I_h symmetry.

Orbitals	Molecule	A_g	F_{1g}	F_{2g}	G_g	H_g	A_u	F_{1u}	F_{2u}	G_u	H_u
s	X_{12}	1				1		1	1		
s	X_{20}	1			1	1		1	1	1	
s	X_{30}	1			1	2		1	1	1	1
s	C_{60}	1	1	1	2	3		2	2	2	2
p	X_{12}	1	1		1	2		2	1	1	1
p	X_{20}	1	1	1	2	3		2	2	2	2
p	X_{30}	1	2	2	3	4		3	3	3	3
p	C_{60}	2	4	4	6	8	1	5	5	6	7
$p\pi$	C_{60}	1	1	1	2	3		2	2	2	2
$p\sigma$	C_{60}	1	3	3	4	5	1	3	3	4	5
d	X_{12}	1	1	1	2	3		2	2	2	2
d	X_{20}	1	2	2	3	5		3	3	3	4
d	X_{30}	2	3	3	5	7	1	4	4	5	6
d	C_{60}	3	7	7	10	13	2	8	8	10	12

TABLE V. Character table for T_h .

T_h	E	$3C_2$	$4C_3$	$4C'_3$	i	$3\sigma_v$	$4S_3$	$4S'_3$	Basis functions
A_g	1	1	1	1	1	1	1	1	$x^2 + y^2 + z^2$
E_g	$\begin{cases} 1 \\ 1 \end{cases}$	1	ω	ω^2	1	1	ω	ω^2	$x^2 + \omega y^2 + \omega^2 z^2$
T_g	3	-1	0	0	3	-1	0	0	$(R_x, R_y, R_z), (yz, zx, xy)$
A_u	1	1	1	1	-1	-1	-1	-1	xyz
E_u	$\begin{cases} 1 \\ 1 \end{cases}$	1	ω	ω^2	-1	-1	$-\omega$	$-\omega^2$	$x^3 + \omega y^3 + \omega^2 z^3$
T_u	3	-1	0	0	-3	1	0	0	(x, y, z)

TABLE VI. Equivalent sites of space group T_h^6

Sites	Notation	Site symmetry	Site coordinates	$\chi^{a.s.}$
4	a	$\bar{3}$	$0,0,0; 0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, 0$	$A_g + T_g$
4	b	$\bar{3}$	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, 0; 0, \frac{1}{2}, 0; 0, 0, \frac{1}{2}$	$A_g + T_g$
8	c	3	$\begin{cases} x, x, x; \frac{1}{2} + x, \frac{1}{2} - x, \bar{x}; \bar{x}, \frac{1}{2} + x, \frac{1}{2} - x; \frac{1}{2} - x, \bar{x}, \frac{1}{2} + x \\ \bar{x}, \bar{x}, \bar{x}; \frac{1}{2} - x, \frac{1}{2} + x, x; x, \frac{1}{2} - x, \frac{1}{2} + x; \frac{1}{2} + x, x, \frac{1}{2} - x \\ x, y, z; \frac{1}{2} + x, \frac{1}{2} - y, \bar{z}; \bar{x}, \frac{1}{2} + y, \frac{1}{2} - z; \frac{1}{2} - x, \bar{y}, \frac{1}{2} + z \\ z, x, y; \frac{1}{2} + z, \frac{1}{2} - x, \bar{y}; \bar{z}, \frac{1}{2} + x, \frac{1}{2} - y; \frac{1}{2} - z, \bar{x}, \frac{1}{2} + y \\ y, z, x; \frac{1}{2} + y, \frac{1}{2} - z, \bar{x}; \bar{y}, \frac{1}{2} + z, \frac{1}{2} - x; \frac{1}{2} - y, \bar{z}, \frac{1}{2} + x \\ \bar{x}, \bar{y}, \bar{z}; \frac{1}{2} - x, \frac{1}{2} + y, z; x, \frac{1}{2} - y, \frac{1}{2} + z; \frac{1}{2} + x, y, \frac{1}{2} - z \\ \bar{z}, \bar{x}, \bar{y}; \frac{1}{2} - z, \frac{1}{2} + x, y; z, \frac{1}{2} - x, \frac{1}{2} + y; \frac{1}{2} + z, x, \frac{1}{2} - y \\ \bar{y}, \bar{z}, \bar{x}; \frac{1}{2} - y, \frac{1}{2} + z, x; y, \frac{1}{2} - z, \frac{1}{2} + x; \frac{1}{2} + y, z, \frac{1}{2} - x \end{cases}$	$A_g + T_g + A_u + T_u$
24	d	1		$\begin{cases} A_g + E_g + 3T_g \\ + A_u + E_u + 3T_u \end{cases}$

stoichiometry M_2C_{60} , or if both tetrahedral and octahedral sites are fully occupied then the composition M_3C_{60} is achieved.²¹ Finally, occupation of the general d sites with T_h^6 symmetry in Table VI results in a stoichiometry M_6C_{60} . Structure determinations for $x \leq 3$ (Ref. 21) indicate a fcc ordering of the fullerene molecules, so our approximate structure is either correct or very closely approximates the real material for $x \leq 3$. However for $x > 3$ both a body-centered-tetragonal phase for $x = 4$ and a body-centered-cubic structure for $x = 6$ have been reported.¹⁸ The body-centered-tetragonal phase²⁰ is a lower-symmetry space group (the C_{60} molecules would occupy sites with C_{2v} symmetry) and is not considered further in this paper.

C. Phonon modes of pristine and doped C₆₀ in space groups T_h^6 and T_h^5

The number of allowed Raman modes for C_{60} in the T_h^6 structure is very large and includes 29 one-dimensional A_g modes, 29 two-dimensional E_g modes, and 87 three-dimensional T_g modes (see Table VIII). The room-temperature experimental Raman spectra^{6,7,10,22} summarized in Table IX, however, suggest that most of the Raman-allowed modes for the T_h^6 space group are very weak or give rise to very small unresolved splittings of the 10 main Raman-allowed modes in the isolated C_{60} molecule.

The simplicity of the observed Raman spectra suggests the perturbative treatment outlined in Table VIII. Starting with the $3 \times 60 - 6$ vibrational degrees of freedom for the free molecule with I_h symmetry (first column of Table VIII), the lower T_h point symmetry in the crystal gives rise to the mode splittings indicated in the second column of Table VIII. When the four C_{60} molecules are placed in the T_h^6 space-group sites, the appropriate mode symmetries are found (see the third column of the table) by taking the direct product of the characters for

the molecular site symmetries of the four balls ($A_g + T_u$) (see the last column of Table VI) with the characters for the vibrational modes for the C_{60} molecule in T_h symmetry (second column).

In addition to the high-frequency modes listed in Table VIII, there are 24 low-frequency modes ($\omega < 200 \text{ cm}^{-1}$) associated with the molecular translational (F_{1u} or T_u) and rotational (F_{1g} or T_g) degrees of freedom of the fullerene molecules

$$(T_g + T_u) \otimes (A_g + T_g) \Rightarrow A_g + E_g + 3T_g \\ + A_u + E_u + 3T_u,$$

where \otimes denotes the direct product. Of these, the acoustic mode is of symmetry T_u , and there are 9 other fullerene displacive modes of symmetries $A_u + E_u + 2T_u$. The 12 fullerene rotational modes have symmetries $T_g + A_g + E_g + 2T_g$. At general points in the Brillouin zone the low-frequency translational and rotational modes will hybridize and form librational modes. It appears unlikely that any of these low-frequency modes have been observed in the experiments reported thus far.^{1,6,7,10}

The symmetry for the T_h^5 bcc space group given in Table VII is based on two molecular units per nonprimitive unit cell at the indicated sites. If a dopant is at an a site, the stoichiometry would be X_1C_{60} , while occupation of the b sites would yield an X_3C_{60} stoichiometry, and occupation of the c sites would yield an X_4C_{60} composition. The X_6C_{60} can be achieved by occupation of either d or e sites, but no definitive experiment has yet been done to distinguish between these two options. The primitive bcc unit cell has only one C_{60} molecule and the mode symmetries are shown in Table VIII. The acoustic mode is of symmetry T_u , and there are three hybridized librational modes of symmetry T_g for the Γ point of the T_h^5 space group.

This symmetry analysis suggests the following mode

TABLE VII. Equivalent sites of space group T_h^5 . For the nonprimitive unit cell multiply $\chi^{a.s.}$ by 2.

Sites	Notation	Site symmetry	Site coordinates: $(0,0,0); (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) +$	$\chi^{a.s.}$
2	a	$m\bar{3}$	0,0,0	A_g
6	b	mmm	$0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, 0$	$A_g + E_g$
8	c	$\bar{3}$	$\frac{1}{4}, \frac{1}{4}, \frac{1}{4}; \frac{1}{4}, \frac{3}{4}, \frac{3}{4}; \frac{3}{4}, \frac{1}{4}, \frac{3}{4}; \frac{3}{4}, \frac{3}{4}, \frac{1}{4}$	$A_g + T_g$
12	d	mm	$\left\{ \begin{array}{l} x, 0, 0; \quad 0, x, 0; \quad 0, 0, x \\ \bar{x}, 0, 0; \quad 0, \bar{x}, 0; \quad 0, 0, \bar{x} \end{array} \right.$	$\left\{ \begin{array}{l} A_g + E_g \\ + T_u \end{array} \right.$
12	e	mm	$\left\{ \begin{array}{l} x, 0, \frac{1}{2}; \quad \frac{1}{2}, x, 0; \quad 0, \frac{1}{2}, x \\ \bar{x}, 0, \frac{1}{2}; \quad \frac{1}{2}, \bar{x}, 0; \quad 0, \frac{1}{2}, \bar{x} \end{array} \right.$	$\left\{ \begin{array}{l} A_g + E_g \\ + T_u \end{array} \right.$
16	f	3	$\left\{ \begin{array}{l} x, x, x; \quad x, \bar{x}, \bar{x}; \quad \bar{x}, x, \bar{x}; \quad \bar{x}, \bar{x}, x \\ \bar{x}, \bar{x}, \bar{x}; \quad \bar{x}, x, x; \quad x, \bar{x}, x; \quad x, x, \bar{x} \end{array} \right.$	$\left\{ \begin{array}{l} A_g + T_g \\ + A_u + T_u \end{array} \right.$
24	g	m	$\left\{ \begin{array}{l} 0, y, z; \quad z, 0, y; \quad y, z, 0; \quad 0, \bar{y}, \bar{z}; \quad \bar{z}, 0, \bar{y}; \quad \bar{y}, \bar{z}, 0 \\ 0, y, \bar{z}; \quad \bar{z}, 0, y; \quad y, \bar{z}, 0; \quad 0, \bar{y}, z; \quad z, 0, \bar{y}; \quad \bar{y}, z, 0 \end{array} \right.$	$\left\{ \begin{array}{l} A_g + E_g \\ + T_g + 2T_u \end{array} \right.$
48	h	1	$\left\{ \begin{array}{l} x, y, z; \quad z, x, y; \quad y, z, x; \quad \bar{x}, \bar{y}, \bar{z}; \quad \bar{z}, \bar{x}, \bar{y}; \quad \bar{y}, \bar{z}, \bar{x} \\ x, \bar{y}, \bar{z}; \quad z, \bar{x}, \bar{y}; \quad y, \bar{z}, \bar{x}; \quad \bar{x}, y, z; \quad \bar{z}, x, y; \quad \bar{y}, z, x \\ \bar{x}, y, \bar{z}; \quad \bar{z}, x, \bar{y}; \quad \bar{y}, z, \bar{x}; \quad x, \bar{y}, z; \quad z, \bar{x}, y; \quad y, \bar{z}, x \\ \bar{x}, \bar{y}, z; \quad \bar{z}, \bar{x}, y; \quad \bar{y}, \bar{z}, x; \quad x, y, \bar{z}; \quad z, x, \bar{y}; \quad y, z, \bar{x} \end{array} \right.$	$\left\{ \begin{array}{l} A_g + E_g + 3T_g \\ + A_u + E_u + 3T_u \end{array} \right.$

TABLE VIII. Brillouin-zone-center vibrational modes for the carbon atoms in space groups T_h^6 and T_h^5 . The modes associated with the dopant atoms must be accounted for separately as described in the text.

I_h	T_h, T_h^{5a}	T_h^{6b}
$2A_g$	$2A_g$	$2A_g + 2T_g$
$3F_{1g}$	$3T_g$	$3T_g + 3(A_g + E_g + 2T_g)$
$4F_{2g}$	$4T_g$	$4T_g + 4(A_g + E_g + 2T_g)$
$6G_g$	$6A_g + 6T_g$	$6(A_g + T_g) + 6(A_g + E_g + 3T_g)$
$8H_g$	$8E_g + 8T_g$	$8(E_g + T_g) + 8(A_g + E_g + 4T_g)$
$1A_u$	$1A_u$	$A_u + T_u$
$4F_{1u}$	$4T_u$	$4T_u + 4(A_u + E_u + 2T_u)$
$5F_{2u}$	$5T_u$	$5T_u + 5(A_u + E_u + 2T_u)$
$6G_u$	$6A_u + T_u$	$6(A_u + T_u) + 6(A_u + E_u + 3T_u)$
$7H_u$	$7E_u + 7T_u$	$7(E_u + T_u) + 7(A_u + E_u + 4T_u)$

^aThe modes associated with translations and rotations of the center of mass of the two C_{60} molecules must also be counted for the space group, giving additional $T_g + T_u$ modes, one of which (T_u) is the acoustic mode.

^bThe modes associated with translations and rotations of the center of mass of the four C_{60} molecules must also be counted for the space group, giving additional $A_g + E_g + 3T_g + A_u + E_u + 3T_u$ modes, one of which (T_u) is the acoustic mode.

scheme for the Raman experiments. The ten main observable Raman modes for solid and alkali-metal-doped C_{60} are the Raman-active molecular modes of the free C_{60} molecule with $2A_g + 8H_g$ symmetries. When placed in the lower T_h symmetry, each of the five-dimensional H_g modes are split into a two-dimensional E_g and a three-dimensional T_g mode. In addition, the $3F_{1g}$, $4F_{2g}$,

and $6G_g$ modes become weakly Raman active because all even-parity modes in T_h symmetry are Raman allowed. The G_g modes are also split as indicated in the second column of Table VIII. Finally when the inversion symmetry-breaking intermolecular interactions are considered, the odd-parity modes are all turned on and further splittings occur. The experiments indicate that the intensities of the odd-parity modes activated by intermolecular interactions are unobservably small, as are most of the splittings of the G - and H -derived modes. Thus the Raman spectra can be interpreted as providing convincing evidence for weak intermolecular C_{60} - C_{60} and C_{60} -dopant coupling.

We now apply these concepts to the interpretation of the observed Raman spectra in C_{60} and $M_x C_{60}$ materials.

III. APPLICATION TO RAMAN EXPERIMENTS

In this section we apply the symmetry analysis of Sec. II to the Raman spectra presented previously.^{6,7,10} To facilitate a discussion of the symmetry properties of these spectra, we list in Table IX the observed frequencies for Raman-active modes in C_{60} and in $M_6 C_{60}$ (where $M=K,Rb,Cs$), including the depolarization ratio $I_{\parallel,\perp}/I_{\parallel,\parallel}$ which we use extensively in the discussion of selection rules. Starting with the Raman spectra for undoped C_{60} ,^{10,14} ten Raman lines ($2A_g + 8H_g$) are predicted from group theory for the C_{60} molecule and ten lines are indeed observed for C_{60} films, implying a very weak C_{60} - C_{60} interaction. Polarization selection rules distinguish the two A_g modes [seen only for the (\parallel, \parallel) polarization] in pristine C_{60} at 493 cm^{-1} (the radial A_g mode) and at 1469 cm^{-1} (the tangential A_g mode), from

TABLE IX. Experimentally observed lattice modes in pristine and alkali-metal-doped C_{60} .

I_h mode	T_h mode	C_{60}		$K_6 C_{60}$		$Rb_6 C_{60}$		$Cs_6 C_{60}$	
		cm^{-1}	$I_{\parallel,\perp}/I_{\parallel,\parallel}$	cm^{-1}	$I_{\parallel,\perp}/I_{\parallel,\parallel}$	cm^{-1}	$I_{\parallel,\perp}/I_{\parallel,\parallel}$	cm^{-1}	$I_{\parallel,\perp}/I_{\parallel,\parallel}$
A_g	A_g	1468.5	0.10	1432.5 ^a	0.13	1432.5	0.10	1433.0	0.10
A_g	A_g	493.0	0.02	502.0	0.10	499.5	0.12	497.5	0.11
H_g	$E_g + T_g^b$	1573.0	0.52	1476.0	0.48	1483.5	0.80	1480.5	0.54
H_g	$E_g + T_g$	1426.0	0.44	$\left\{ \begin{array}{l} 1383.5 \\ 1237.0 \end{array} \right.$	$\left\{ \begin{array}{l} 0.50 \\ 0.88 \end{array} \right.$	$\left\{ \begin{array}{l} 1419.5 \\ 1385.0 \end{array} \right.$	$\left\{ \begin{array}{l} 0.14 \\ 0.60 \end{array} \right.$	$\left\{ \begin{array}{l} 1421.0 \\ 1384.0 \end{array} \right.$	$\left\{ \begin{array}{l} 0.28 \\ 0.52 \end{array} \right.$
H_g	$E_g + T_g$	1248.0							
H_g	$E_g + T_g$	1099.0	0.38	$\left\{ \begin{array}{l} 1120.0 \\ 1094.0 \end{array} \right.$	$\left\{ \begin{array}{l} 0.38 \\ 0.42 \end{array} \right.$	$\left\{ \begin{array}{l} 1120.5 \\ 1092.0 \end{array} \right.$	$\left\{ \begin{array}{l} 0.35 \\ 0.78 \end{array} \right.$	$\left\{ \begin{array}{l} 1118.0 \\ 1090.0 \end{array} \right.$	$\left\{ \begin{array}{l} 0.58 \\ 0.91 \end{array} \right.$
H_g	$E_g + T_g$	772.5							
H_g	$E_g + T_g$	708.5	0.40	$\left\{ \begin{array}{l} 676.0 \\ 658.0 \end{array} \right.$	$\left\{ \begin{array}{l} 0.00 \\ 0.49 \end{array} \right.$	$\left\{ \begin{array}{l} 676.5 \\ 657.5 \end{array} \right.$	$\left\{ \begin{array}{l} 0.00 \\ 0.74 \end{array} \right.$	$\left\{ \begin{array}{l} 678.0 \\ 658.5 \end{array} \right.$	$\left\{ \begin{array}{l} 0.00 \\ 0.47 \end{array} \right.$
H_g	$E_g + T_g$	430.5							
H_g	$E_g + T_g$	270.0	0.52	$\left\{ \begin{array}{l} 419.5 \\ 281.0 \end{array} \right.$	$\left\{ \begin{array}{l} 0.75 \\ 0.91 \end{array} \right.$	$\left\{ \begin{array}{l} 421.5 \\ 277.0 \end{array} \right.$	$\left\{ \begin{array}{l} 0.61 \\ 0.85 \end{array} \right.$	$\left\{ \begin{array}{l} 424.0 \\ 272.5 \end{array} \right.$	$\left\{ \begin{array}{l} 0.67 \\ 0.48 \end{array} \right.$
H_g	$E_g + T_g$								

^a Raman lines at 1430 and 1447 cm^{-1} for $K_6 C_{60}$ and $K_3 C_{60}$, respectively, have been reported by Haddon *et al.* (Ref. 1).

^b For the modes that show a splitting, it would be expected that the mode with the smaller value of $I_{\parallel,\perp}/I_{\parallel,\parallel}$ would correspond to the E_g symmetry mode.

the eight H_g modes which are seen for both (\parallel, \parallel) and (\parallel, \perp) polarizations.

Referring to the spectra for the three M_6C_{60} samples in Table IX, we see almost the same spectrum, independent of whether the alkali metal is K, Rb, or Cs. Of particular interest also is the similarity of these three spectra to that for C_{60} . We thus start our symmetry analysis of the M_6C_{60} spectra in terms of the ten lines that dominate the C_{60} spectrum. We further note that several of the lines in the M_6C_{60} spectra down shift in frequency relative to that for pristine C_{60} , and a few of the M_6C_{60} lines split.

It should be remarked that the Raman line shapes for all the modes in C_{60} and M_6C_{60} are Lorentzian and not Gaussian. A Gaussian line shape results from inhomogeneous broadening from a random distribution of defects, such as might arise from incomplete doping of M atoms or from oxygen uptake. The Lorentzian line shapes observed here are therefore consistent with the view that intr fullerene C-C interactions dominate the Raman-active vibrations. Lower-frequency Raman-active modes associated with interfullerene librational motion are expected, but have not yet been reported.

The symmetry selection rule for the A_g lines in I_h or T_h symmetry is that A_g modes are seen only for the (\parallel, \parallel) polarization and not for the (\parallel, \perp) polarization. We note that the radial A_g mode in pristine C_{60} is strongly polarized; i.e., $I_{\parallel, \perp}/I_{\parallel, \parallel} = 0.02$. However, the polarization for the corresponding tangential A_g mode is only $I_{\parallel, \perp}/I_{\parallel, \parallel} = 0.10$, suggesting that the symmetry is only approximately T_h for the C_{60} films being measured experimentally.⁷ Thus, the true symmetry for these C_{60} materials is lower than T_h and the deviation of the selection rule from ideal T_h local symmetry provides an estimate of the magnitude of the symmetry-lowering perturbation. Nevertheless, for pristine solid C_{60} , the fullerene-fullerene interaction is sufficiently weak so that none of the splittings predicted by Table VIII are seen, and the observed spectral features are dominated by interactions with I_h symmetry.

As was stated above, the doping of C_{60} with an alkali metal M to the M_6C_{60} level has only a small effect on the Raman spectra for $M = K, Rb, Cs$.^{6,7} No splittings or changes in polarization selection rules are found for the tangential and radial A_g modes, except with regard to the polarization selection rules. For the tangential A_g mode, the observed polarization ratio remains at $I_{\parallel, \perp}/I_{\parallel, \parallel} \simeq 0.10$ both for the pristine and for the M_6C_{60} samples, whereas the strong selection rule for the radial A_g mode is weakened to the $I_{\parallel, \perp}/I_{\parallel, \parallel} \simeq 0.10$ level as a result of the alkali-metal doping, similar in magnitude to that of the tangential A_g mode. This violation of the polarization selection rule is consistent with a change in the fullerene-alkali-metal distances during the radial vibrations and suggests that the symmetry-lowering perturbation is most sensitive to this change in the fullerene-alkali-metal distances. The softening of the tangential A_g mode and the stiffening of the radial A_g mode upon alkali-metal doping can be explained by charge-transfer-related effects.²³

Of the eight H_g -derived modes in C_{60} , three do not show any measurable splitting, and merely soften as a

result of charge transfer.⁷ We argue that in these cases the T_g - E_g splitting is too small to be observable. The observation of these modes for both \parallel, \parallel and \parallel, \perp polarizations is also consistent with this interpretation. For the remaining five H_g modes, the splitting is small for the two lowest-frequency H_g modes; for these H_g -derived modes, small but significant polarization effects are observed, presumably because of hybridization of the T_g and E_g partners. This is once again associated with the symmetry in the materials under observation being lower than T_h . The third H_g mode derived from the H_g mode at 708.5 cm^{-1} in pristine C_{60} is strongly down shifted and strongly split, and shows a strong polarization selection rule for the E_g mode which is not down shifted as much as the T_g mode. We further note that the down shift for the E_g mode is less than that for the T_g mode, consistent with a larger component of bond stretching relative to bond bending for the E_g mode.^{7,11} The H_g mode derived from the 1099-cm^{-1} mode in C_{60} is split without much change in center frequency. The small degree of polarization for these components is comparable to that observed for the two lowest-frequency lines, presumably because of the hybridization of the T_g and E_g partners associated with the symmetry-lowering perturbation. Finally the modes derived from the 1426-cm^{-1} mode in C_{60} are again significantly down shifted, exhibit a large splitting, and a significant polarization selectively for the E_g mode, which shows much less softening than the T_g mode.

In some regions of the sample where partially filled molecular orbitals occur, a Jahn-Teller distortion of the doped fullerene may be one reason for a doping-induced symmetry-lowering effect that gives rise to a small violation of the Raman selection rule for the E_g and A_g modes. A single electron transferred to a C_{60} molecule is expected to result in a Jahn-Teller distortion of the molecule and thus to lower the symmetry of that lattice site. Such a Jahn-Teller distortion of the molecule has been considered by Saito and Oshiyama^{24,25} and has been estimated to have a small effect on the electronic structure.

The Jahn-Teller distortion also offers a possible theoretical reason for the difficulty in placing a single metal atom in the center of the C_{60} icosahedron. This is because the molecular orbitals which would be occupied by the electron transfer from the inserted atom would be only partly occupied and the Jahn-Teller distortion of the molecule which lowers the symmetry and removes the degeneracy of the partially occupied molecular orbital would then squeeze the atom out of the center of the icosahedron. This argument would imply that atoms which either do not donate electrons (e.g., rare gases) or which have $4f$ orbitals (e.g., La) and hence do not make significant electron transfers are more likely to occupy the center site of the C_{60} .

All of the H_g modes of the C_{60} molecule would be expected to split in the lower T_h symmetry of solid C_{60} and its related metal-doped compounds. Only five of the H_g modes were found to split by measurable amounts. Two of the H_g modes which show relatively large frequency splittings and softening did show polarization effects for

the upper-frequency E_g component, which softened much less than the lower-frequency T_g component, presumably due to the dominance of bond-stretching displacements for the E_g component, which would not be expected to soften as much as the bond-bending displacements associated with the lower-frequency T_g component.

The simplicity of the Raman spectra for C_{60} and M_6C_{60} films implies the importance of experimental polarization studies of the Raman spectra, especially in single-crystal samples.

Note added in proof. Recent experiments on the dependence of the Raman spectrum on laser power indicate that the lower symmetry which is suggested by the partial violation of the polarization selection rule for the A_g

mode at 1468.5 cm^{-1} arises from optical damage which induces a local lowering of symmetry. For laser powers $\leq 2.5\text{ W/cm}^2$, a polarization ratio of $I_{\parallel,\perp}/I_{\parallel,\parallel} \simeq 0.02$, within the accuracy of the polarization leakage, has been observed for this mode [P.C. Eklund, Ping Zhou, Kai-An Wang, G. Dresselhaus, and M.S. Dresselhaus (unpublished)].

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