

## Hindered rotation of solid $^{12}\text{C}_{60}$ and $^{13}\text{C}_{60}$

R. Saito

*Department of Electronics Engineering, University of Electro-Communications, Chofugaoka, Chofu, 182 Tokyo, Japan*

G. Dresselhaus

*Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

M. S. Dresselhaus

*Department of Electrical Engineering and Computer Science and Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

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Hindered rotation is combined with the vibrations of a  $\text{C}_{60}$  molecule and is discussed in the context of icosahedral symmetry. A large difference is predicted for the occurrence of vibrations and rotations between a pure  $^{12}\text{C}_{60}$  molecular solid and a solid containing molecules with the  $^{13}\text{C}$  isotope.

### I. INTRODUCTION

Fullerene  $\text{C}_{60}$  has attracted much interest in many fields of science as another form of carbon and an aromatic molecule with high symmetry.<sup>1-3</sup>  $\text{C}_{60}$  belongs to the highest symmetry point group, icosahedral symmetry  $I_h$ , which has 120 symmetry operations. The high symmetry of the molecule introduces many restrictions on the symmetry-allowed molecular motions, resulting from the Pauli principle, or the statistics of the particles. The absence of certain motions could result in a singularity in the specific heat at very low temperature or anomalies in the intensity of specific features in the Raman or infrared (IR) spectra of  $\text{C}_{60}$  molecules.

The natural abundance of the isotope  $^{13}\text{C}$  is 1.11% and the remaining 98.89% of the carbon atoms are  $^{12}\text{C}$ . If we use this natural abundance for the atomic species, 51.2% of  $\text{C}_{60}$  molecules are pure  $^{12}\text{C}_{60}$ , 34.5% of the  $\text{C}_{60}$  molecules contain one  $^{13}\text{C}$ , 11.4% of the  $\text{C}_{60}$  molecules contain two  $^{13}\text{C}$  and the remaining 2.9% have a larger number of  $^{13}\text{C}$  atoms.<sup>4</sup> If we prepare as pure a sample of  $^{12}\text{C}$  (or  $^{13}\text{C}$ ) atoms as possible, we can get purer  $^{12}\text{C}_{60}$  (or  $^{13}\text{C}_{60}$ ) molecules than would be expected by their natural abundance. A pure  $^{12}\text{C}_{60}$  molecular solid is especially interesting in the sense that it has no nuclear spin  $\mathcal{I}_N$ , and this affects the Pauli-allowed rotations and vibrations greatly, as discussed in this paper.

A simple example of symmetry-induced restricted motion is the motion of the hydrogen molecule.<sup>5</sup> When we consider a deuteron D, with nuclear spin unity ( $\mathcal{I}_N = 1$ ), three different molecules of hydrogen  $\text{H}_2$ ,  $\text{D}_2$ , and HD can be formed. Since H and D nuclei are fermions and bosons, respectively, the total wave functions of  $\text{H}_2$  and  $\text{D}_2$  molecules should be odd and even, respectively, by permutation of the two nuclei. This fact restricts the rotation of  $\text{H}_2$  and  $\text{D}_2$  molecules for which the quantum number of angular momentum of the molecule  $\ell$  is odd or even, depending on the total nuclear spin value  $\mathcal{I}_N$ .

The situation for  $\text{C}_{60}$  is essentially the same as that for the hydrogen molecule since the  $^{12}\text{C}$  and  $^{13}\text{C}$  nuclei are bosons and fermions, respectively. The present paper describes the symmetry-allowed rotational and also rotational-vibrational excitations for a  $^{12}\text{C}_{60}$  molecular solid containing only  $^{12}\text{C}$  isotopes. This symmetry restriction should affect the specific heat at low temperature, the Raman and IR spectra, and the characteristics of the isotope effect in the superconducting transition temperature observed in doped  $\text{C}_{60}$  solids.

The basic idea of rotations and vibrations for the isolated  $\text{C}_{60}$  molecule has already been discussed by Harter *et al.*,<sup>4,6,7</sup> who calculated the nuclear spin weight of  $^{13}\text{C}_{60}$  and discussed the rotovibrational spectra. In this paper we first focus our attention on the effect of isotopic  $^{12}\text{C}$  purity on the Raman and IR spectra for  $^{12}\text{C}_{60}$ . For this purpose we calculate in Sec. II the probability for all possible vibrations which belong to a given irreducible representation of  $I_h$ . Then we apply those group theoretical results to various physical properties in Sec. III. Finally, conclusions are given in Sec. IV.

### II. HINDERED ROTATION OF $^{12}\text{C}_{60}$ AND $^{13}\text{C}_{60}$

Differences in the symmetry of the  $^{12}\text{C}$  and  $^{13}\text{C}$  nuclei in a  $\text{C}_{60}$  molecule are expected to be relevant to the rotational motion of the molecule, as shown below. The statistics for the carbon nuclei restrict the allowed permutation symmetry operations of the total wave function for all the carbon atoms in the  $\text{C}_{60}$  molecule  $\Psi$ , where  $\Psi$  can be expressed by

$$\Psi = \Psi_{\text{el}} \Psi_{\text{vib}} \Psi_{\text{rot}} \Psi_{\text{ns}}, \quad (1)$$

in which  $\Psi_{\text{el}}$ ,  $\Psi_{\text{vib}}$ ,  $\Psi_{\text{rot}}$ , and  $\Psi_{\text{ns}}$  refer, respectively, to the electronic, vibrational, rotational, and nuclear spin factors. The ground state electronic structure of a  $\text{C}_{60}$

molecule requires  $\Psi_{\text{el}}$  to have  $A_g$  symmetry.

In the case of  $^{12}\text{C}_{60}$ , the total wave function  $\Psi$  should be totally symmetric for any permutations of the carbon nuclei in the  $^{12}\text{C}_{60}$  molecule because each  $^{12}\text{C}$  nucleus is a boson with zero spin angular momentum ( $\mathcal{I}_N = 0$ ). In contrast, the  $^{13}\text{C}_{60}$  nuclei have totally antisymmetric states for an odd number of nuclear exchanges since a  $^{13}\text{C}$  nucleus is a fermion ( $\mathcal{I}_N = 1/2$ ). For a  $\text{C}_{60}$  molecule which contains both  $^{12}\text{C}$  and  $^{13}\text{C}$  isotopes, the proper statistics should be applied to the permutations among the  $^{12}\text{C}$  atoms and among the  $^{13}\text{C}$  atoms. Furthermore, there is no restriction regarding the statistics for the permutation between  $^{12}\text{C}$  and  $^{13}\text{C}$  atoms since each is considered to be a different particle. (However, such exchanges are not symmetry operations.)

For simplicity we consider primarily  $^{12}\text{C}_{60}$  and  $^{13}\text{C}_{60}$  molecules in this paper, i.e.,  $\text{C}_{60}$  molecules consisting only of  $^{12}\text{C}$  isotopes or of  $^{13}\text{C}$  isotopes. Because of the icosahedral symmetry of the molecule  $I_h$ , many restrictions occur, resulting from this high symmetry. Any symmetry operation of  $I_h$  can be expressed by a permutation of 60 elements so that the group  $I_h$  is a subgroup of the symmetric group  $S(60)$ . Thus we must consider the symmetries of the total wave function  $\Psi$  under the permutations which belong to  $I_h$ .

The cases considered in this section, where symmetry requirements for the  $\text{C}_{60}$  molecules are important, include the following: in Sec. II A free rotation in vacuum, in Sec. II B vibration-rotation spectra in a  $\text{C}_{60}$  molecule, in Sec. II C librations in solid  $\text{C}_{60}$ , and in Sec. II D lower symmetry cases. The case of Sec. II A shows the greatest number of restrictions to molecular rotations for any molecule, because of the high symmetry of  $\text{C}_{60}$ , so that many rotational states are symmetry forbidden and consequently are suppressed in the observed spectra. In Sec. II B we discuss the allowed vibrations for the rotating molecule. In Sec. II C we discuss the application of Secs. II A and II B to solid  $\text{C}_{60}$ , including the implication of the symmetry restrictions on Raman experiments in solid  $\text{C}_{60}$ , where some librational modes at about  $20\text{ cm}^{-1}$  are observed.<sup>8</sup> The librational modes all have even parity and some librations are symmetry forbidden for  $^{12}\text{C}_{60}$ . Finally, in Sec. II D we briefly mention isotope effects in cases of lower symmetry such as  $^{13}\text{C}_1^{12}\text{C}_{59}$  and  $^{13}\text{C}_2^{12}\text{C}_{58}$ .

#### A. Free rotation in vacuum

Here we consider the free rotation of a  $\text{C}_{60}$  molecule in vacuum. Since a  $\text{C}_{60}$  molecule has a set of three  $C_2$  axes which are perpendicular to each other, the principal moments of inertia  $I_1$ ,  $I_2$ , and  $I_3$  are equal ( $I_1 = I_2 = I_3 = I_M$ ) and  $I_M$  for a  $\text{C}_{60}$  molecule is  $1.0 \times 10^{-43}\text{ kg m}^2$ . Thus the rotation of a  $\text{C}_{60}$  molecule corresponds to the problem of a spherical rotor which is quantized by angular momentum  $J$  and its two components  $m$  ( $m = -J, \dots, J$ ) and  $k$  ( $k = -J, \dots, J$ ). The components  $m$  and  $k$  are, respectively, the  $z$  components of the angular momentum in a coordinate system at rest and components of angular momentum along the principal axis of inertia.<sup>9-11</sup>

The rotational energy of a spherical rotor is given by

$$\frac{\hbar^2}{2I_M} J(J+1) = 3.3 \times 10^{-2} J(J+1) \text{ (K)}. \quad (2)$$

It is noted that the degeneracy for a  $J$  value is not  $(2J+1)$  but  $(2J+1)^2$ , because of the two quantum numbers  $m$  and  $k$ . Since the lowest energy for intramolecular vibrations is on the order of 100 K, we need only consider rotational motion, if the molecule is in vacuum at low temperature ( $< 10\text{ K}$ ).

In the case of  $^{12}\text{C}_{60}$ , there is no nuclear spin in  $^{12}\text{C}$  and thus  $\Psi_{\text{ns}}$  transforms as  $A_g$ . Using Eq. (1) and the fact that  $\Psi_{\text{el}}$ ,  $\Psi_{\text{vib}}$ , and  $\Psi_{\text{ns}}$  all transform as  $A_g$ , the rotational states  $\Psi_{\text{rot}}$  must also have  $A_g$  symmetry,

$$\Psi_{\text{rot}} \rightarrow A_g.$$

Thus, the rotational motion is restricted to  $J$  values which contain the irreducible representation  $A_g$  of point group  $I_h$ . In Table I we show the decomposition of ro-

TABLE I. Decomposition of angular momenta basis functions in the full rotation group into irreducible representations of the group  $I$ .

$J$	$\Gamma_1(A)$	$\Gamma_2(F_1)$	$\Gamma_3(F_2)$	$\Gamma_4(G)$	$\Gamma_5(H)$
0	1				
1		1			
2					1
3			1	1	
4				1	1
5		1	1		1
6	1	1		1	1
7		1	1	1	1
8			1	1	2
9		1	1	2	1
10	1	1	1	1	2
11		2	1	1	2
12	1	1	1	2	2
13		1	2	2	2
14		1	1	2	3
15	1	2	2	2	2
16	1	2	1	2	3
17		2	2	2	3
18	1	1	2	3	3
19		2	2	2	4
20	1	2	2	2	4
21	1	3	2	3	3
22	1	2	2	3	4
23		2	3	3	4
24	1	2	2	4	4
25	1	3	3	3	4
26	1	3	2	3	5
27	1	3	3	4	4
28	1	2	3	4	5
29		3	3	4	5
30	2	3	3	4	5
31	1	4	3	4	5
32	1	3	3	4	6
33	1	3	4	4	5
34	1	3	3	4	6
35	1	4	4	4	6
36	2	4	3	5	6

tational states with various  $J$  values into the irreducible representations of the group  $I$ , in which  $I$  is a subgroup of  $I_h$  ( $I \otimes i$ ) and  $i$  is the inversion group. It is noted that the degeneracy  $(2J + 1)$ , which comes from the  $k$  quantization, is not included in the table. The degeneracy of the rotational states in an irreducible representation of  $I_h$  is the product of  $(2J + 1)$  and the dimension of the irreducible representation. The even ( $g$ ) and odd ( $u$ ) parity states for  $I_h$  for a given  $\Gamma$  irreducible representation of  $I$  are given for even and odd values of  $J$ , respectively.

From Table I it follows that the possible  $J$  values which have  $A_g$  symmetry are  $J = 0, 6, 10, 12, 16, \dots$ . The lowest rotational excited states thus must have  $J = 6$ , which corresponds to the low temperature 1.6 K. It is interesting that all rotations from  $J = 1$  to  $J = 5$  are not allowed in the  $^{12}\text{C}_{60}$  molecule because of the Pauli principle.

In  $^{13}\text{C}_{60}$ , each  $^{13}\text{C}$  nucleus has a nuclear spin  $\mathcal{I}_N = 1/2$  and thus in the  $^{13}\text{C}_{60}$  molecule there are  $2^{60}$  nuclear spin states from  $\mathcal{I}_{\text{tot}} = 0$  to  $\mathcal{I}_{\text{tot}} = 30$ . The decomposition of  $2^{60}$  nuclear spin states into irreducible representations of  $\mathcal{I}_{\text{tot}} = I_N$  has been examined by Harter and Reimer.<sup>4</sup> We also calculate this decomposition, but by another simple method, which is shown in the Appendix. Our calculated results show that the statistical weight for each irreducible representation of  $I_h$  for all  $2^{60}$  states is very well approximated by the dimension of the irreducible representation as shown in Table II. When the nuclear states belong to the  $\Gamma$  irreducible representation of  $I_h$ , the rotational states should contain the same  $\Gamma$  states if there is no vibration because the direct product of the basis functions for the rotational states and the nuclear states must contain the totally symmetric representation  $A_g$

$$\Psi_{\text{rot}}\Psi_{\text{ns}} \rightarrow A_g.$$

Here it is noted that only totally antisymmetric states belong to the  $A_g$  irreducible representation of  $I_h$  because all operations of  $I_h$  are even permutations and the totally antisymmetric wave function does not change sign under even permutations.

For example, the  $J = 0$  rotation corresponds to  $A_g$  symmetry and the corresponding  $A_g$  nuclear spin states occur with probability  $1/32$  as shown in Table II. The  $J = 1$  rotation corresponds to the irreducible representation  $F_{1u}$  with a probability of  $3/32$ , and so on. Here we assume that all nuclear states are equally probable, which is a reasonable assumption because the nuclear spin-spin interaction between different atoms is very weak and all the nuclear spin states have almost the same energy on the scale of molecular rotations. Thus this assumption is applicable even at very low temperature (0.01 K).

TABLE II. Decomposition of nuclear spin states of  $^{13}\text{C}_{60}$  into irreducible representations of  $I_h$ .

$\mathcal{I}$	$A$	$F_1$	$F_2$	$G$	$H$	Total
$(g)$	1	3	3	4	5	16
$(u)$	1	3	3	4	5	16
$(g + u)$	2	6	6	8	10	32

It is interesting that different  $J$  values appear for the various  $^{13}\text{C}_{60}$  molecules according to their nuclear spin states. In the case of carbon, the spin-orbit interaction is very small and the interaction between  $\text{C}_{60}$  molecules is relatively small, so that the nuclear spin states have relatively long lifetimes, which depend on the magnitude of the spin-lattice, spin-spin, and spin-orbit interactions.

In Fig. 1 the specific heat of a  $^{12}\text{C}_{60}$  molecule (solid line), a  $^{13}\text{C}_{60}$  molecule (dashed line), and a  $\text{C}_{60}$  molecule without symmetry (dotted line) are plotted as a function of  $T$ . The inset shows the same plots in the very low temperature region. If we do not consider any symmetry effects, the specific heat per molecule is saturated at  $3k_B/2$  at very low temperatures (0.05 K). On the other hand,  $^{13}\text{C}_{60}$  and  $^{12}\text{C}_{60}$  both have a large Schottky-type peak in the specific heat, reflecting the energy gap of the allowed rotational levels discussed above.

Thus a large difference in the rotational states is expected between  $^{12}\text{C}_{60}$  and  $^{13}\text{C}_{60}$  molecules. When we consider vibrations at higher temperatures, a comparable situation is found, but with a different probability distribution, as is shown in the next section.

## B. Vibration-rotational modes of a $\text{C}_{60}$ molecule

For  $^{12}\text{C}_{60}$  and  $^{13}\text{C}_{60}$  molecules which have  $I_h$  symmetry, there are 46 distinct vibrational modes among the 174 vibrational degrees of freedom, for which the relative occurrences of the irreducible representations  $\Gamma$  are given in Table III.<sup>12</sup> The relative occurrences are approximately given by the ratio of the dimensions of each ir-

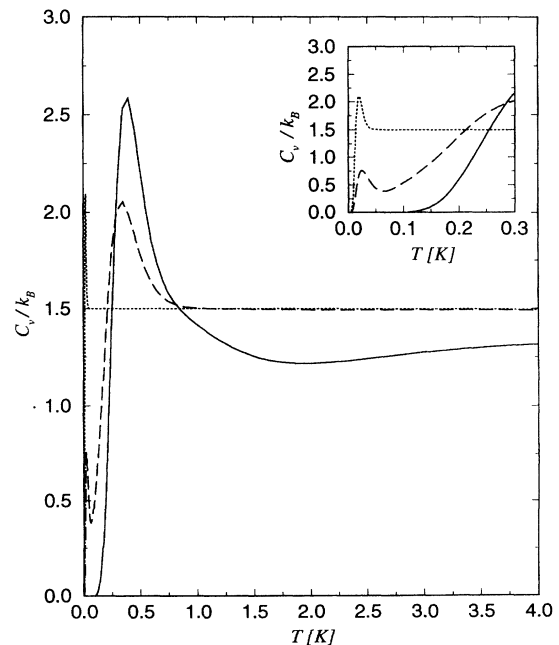


FIG. 1. Specific heat of a  $\text{C}_{60}$  molecule.  $^{12}\text{C}_{60}$  (solid line),  $^{13}\text{C}_{60}$  (dashed line), and  $\text{C}_{60}$  without symmetry (dotted line) plotted as a function of  $T$ . Inset shows behavior in the very low temperature region.

TABLE III. The number of distinct modes for each symmetry type for the 46 distinct vibrational modes of icosahedral  $\text{C}_{60}$  (group  $I_h$ ).

Vibration mode	$A$	$F_1$	$F_2$	$G$	$H$	Total
( $g$ )	2	3	4	6	8	23
( $u$ )	1	4	5	6	7	23
( $g + u$ )	3	7	9	12	15	46

reducible representation. It is noted that the number of  $g$  and  $u$  modes (23) is the same for even ( $g$ ) and odd ( $u$ ) vibrations, since  $I_h$  is the direct product of the  $I$  and  $i$  subgroups, and pure rotational and translational degrees of freedom have the symmetries  $F_{1g}$  and  $F_{1u}$ , respectively.

If a vibrational mode with  $\Gamma$  symmetry exists, the direct product of the irreducible representations for the rotation and nuclear spin must contain the  $\Gamma$  symmetry:

$$\Psi_{\text{rot}} \Psi_{\text{ns}} \rightarrow \Gamma.$$

In the case of  $^{12}\text{C}_{60}$ , since  $\Psi_{\text{ns}}$  transforms as  $A_g$ , then  $\Psi_{\text{rot}}$  must have  $\Gamma$  symmetry. For example, if there is a vibrational mode with  $H_g$  symmetry, possible  $J$  values are  $J = 2, 4, 6, 8, \dots$  as is shown in Table I, when parity is also considered. If the vibrational mode has  $F_{1g}$  symmetry, possible  $J$  values are  $J = 6, 10, 12, \dots$ . It is stressed that in the crystalline solid, the rotations that are hindered depend on the symmetry  $\Gamma$  of the vibrational mode. On the other hand, if a  $^{12}\text{C}_{60}$  molecule is in rotation with a  $J = 4$  rotational mode, the allowed vibrational modes can have only  $G_g$  and  $H_g$  symmetries. In this way, the rotational and vibrational modes are strongly coupled to one another by their symmetry in free rotation.

In the case of  $^{13}\text{C}_{60}$ , all rotations that are hindered in  $^{12}\text{C}_{60}$  occur for some nuclear spin states. The situation may be complicated since there is a distribution of nuclear spin states. For example, the  $J = 1$  ( $F_{1u}$ ) rotational states associated with  $F_{1u}$  vibrational states are possible with a probability of (35/288), which arises from the direct product  $F_{1u} \otimes F_{1u} = A_g + F_{2g} + H_g$  and summing the probabilities for each symmetry type: (1)  $A_g$  nuclear states ( $1/9 \times 1/32$ ), (2)  $F_{2g}$  states ( $3/9 \times 3/32$ ), or (3)  $H_g$  states ( $5/9 \times 5/32$ ), thus yielding a total of 35/288.

At reasonably high temperature relative to rotational energies, large  $J$  values ( $J = 30$ , for example) are possible and the distribution for  $J$  for large  $J$  is almost independent of the  $J$  value. The possibility of finding a  $\Gamma$  irreducible representation for the rotational states may then approach the value of the degeneracy of the irreducible representation, as shown in Table IV. In this table the actual numbers of irreducible representations from  $J = 0$  to  $J = 30$  are listed in parentheses, with each entry weighted by the angular momentum degeneracy factor ( $2J + 1$ ). It should be noted that the ratios of the numbers in parentheses are strongly related to the degeneracy factors for each of the mode symmetries.

Using the approximation for the high temperature limit, the probability of finding a given  $\Gamma$  vibration, which is itself determined by the probability of exciting a given

TABLE IV. Average numbers of irreducible representations for rotations in the high temperature limit (upper number). The lower number gives the number of times a given irreducible representation appears between  $J = 0$  and  $J = 30$ , weighted by the degeneracy factor  $(2J + 1)^2$ .

$\nu_{\text{rot}}$	$A$	$F_1$	$F_2$	$G$	$H$	Total
( $g$ )	1	3	3	4	5	16
	8436	47203	47803	56398	69196	229036
( $u$ )	1	3	3	4	5	16
	23301	43925	44765	65545	86205	263741
( $g + u$ )	2	6	6	8	10	32
	31737	91128	92568	121943	155401	492777

rotation, is given in Table V for  $^{12}\text{C}_{60}$ . In this table we see that the probabilities for the allowed vibrations are inversely proportional to the dimensionality of the irreducible representation. The corresponding results for the  $^{13}\text{C}_{60}$  vibrations are given in Table VI. For example, in the case of  $^{12}\text{C}_{60}$ , the  $F_{1g}$  vibration is possible only when the rotation level has  $F_{1g}$  symmetry, whose probability is  $3/32$ . In the direct product of  $F_{1g} \otimes F_{1g} = A_g + F_{1g} + H_g$ , the one dimensional irreducible representation  $A_g$  appears only once out of the nine dimensions. Thus the total probability becomes  $(1/9 \times 3/32)$ . It is not necessary for the total sum of the probabilities for all irreducible representations for the vibration to sum to unity. In the case of  $^{13}\text{C}_{60}$ , the  $H_g$  irreducible representation appears 42 times in the direct product  $\Gamma_{\text{rot}} \otimes \Gamma_{\text{ns}}$  whose total dimension is  $32 \times 32 = 1024$ . Thus the probability of finding  $H_g$  in the direct product of  $\Gamma_{\text{rot}} \otimes \Gamma_{\text{ns}}$  is  $5 \times 42/1024$  in the high temperature limit. Using the fact that  $H_g \otimes H_g = A_g + F_{1u} + F_{1g} + 2G_g + 2H_g$ , the probability that the total wave function contains  $A_g$  symmetry when the vibration has  $H_g$  symmetry is  $1/25 \times 5 \times 42/1024$ .

Again it is important to note that there is a difference between the  $^{12}\text{C}_{60}$  and  $^{13}\text{C}_{60}$  molecules regarding the occurrence of vibrational states at high temperature for the equi-weighted averaged rotation. In the case of a  $\text{C}_{60}$  molecule, since all IR-active modes have the same  $F_{1u}$  symmetry, the relative intensity ratio for the four IR-active modes is not affected by the isotope effect. However, the expected intensities for the IR-active modes of  $^{12}\text{C}_{60}$  are predicted to be different from those for  $^{13}\text{C}_{60}$  because of the different probabilities given in Tables V and VI. As for Raman-active modes, both the symmetries  $A_g$  and  $H_g$  are allowed and the intensity ratio for the Raman lines with  $A_g$  and  $H_g$  symmetries will be different for  $^{12}\text{C}_{60}$  and  $^{13}\text{C}_{60}$ , in accordance with Tables V

TABLE V. Probability of allowed vibrations  $\nu(^{12}\text{C}_{60})$  for the  $^{12}\text{C}_{60}$  molecule in averaged rotational states with the indicated symmetries.

$\nu_{\text{vib}}(^{12}\text{C}_{60})$	$A$	$F_1$	$F_2$	$G$	$H$
( $g$ )	1/32	1/96	1/96	1/128	1/160
( $u$ )	1/32	1/96	1/96	1/128	1/160

TABLE VI. Probability of allowed vibrations  $\nu(^{13}\text{C}_{60})$  for the  $^{13}\text{C}_{60}$  molecule in averaged rotational states.

$\nu_{\text{vib}}(^{13}\text{C}_{60})$	$A$	:	$F_1$	:	$F_2$	:	$G$	:	$H$
( $g$ )	5/512	:	13/1536	:	13/1536	:	17/2048	:	21/2560
( $u$ )	5/512	:	13/1536	:	13/1536	:	17/2048	:	21/2560

and VI.

It is also noted that in the above treatment there is no consideration of the canonical distribution of the vibrations according to their temperature dependence, which would contain a Boltzmann factor  $\exp(-E_{\text{vib}}/k_B T)$ . This result for the probability of the occurrence of a particular vibration only reflects the statistics of the nuclear spin states and the rotational states. It is important also to consider the hindered rotations imposed by the isotopic degrees of freedom, especially when the isotope effect for the superconducting transition temperature is considered.

### C. Librational motion in solid and doped $\text{C}_{60}$

In solid  $\text{C}_{60}$ , the translational and rotational modes are hybridized and form librational modes. The space groups of alkali-metal-doped  $\text{C}_{60}$  and of pure  $\text{C}_{60}$  below the ordering temperature (261 K) (Ref. 13) are determined as  $T_h^5$  and  $T_h^6$ , respectively, by x-ray diffraction.<sup>14,15</sup> There are four  $\text{C}_{60}$  molecules per unit cell of the simple cubic structure for the pure  $\text{C}_{60}$  solid, yielding  $6 \times 4 = 24$  librational modes (or dispersion relations) per unit cell. Hereafter, we consider only the  $\Gamma$  point of the Brillouin zone, which is relevant to the observation of the librational modes by Raman spectroscopy. The Raman-active modes in the cubic solid  $\text{C}_{60}$  have symmetries  $A_g$ ,  $E_g$ , and  $T_g$  of the  $T_h$  space group at the  $\Gamma$  point.

The 24 intermolecular modes at the  $\Gamma$  point of the Brillouin zone, associated with the molecular translational ( $T_u$ ) and rotational ( $T_g$ ) degrees of freedom for the fullerene molecules, are decomposed into the irreducible representations of the space group  $T_h$  by taking the direct product of ( $T_g + T_u$ ) with the irreducible representations of the atomic sites ( $A_g + T_g$ ) for the group  $T_h$ ,

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

Among the 12 modes with odd parity, 3 modes with  $T_u$  symmetry are acoustic modes, which have zero energy at the  $\Gamma$  point, and the other 9 odd parity modes  $A_u + E_u + 2T_u$  are fullerene displacive modes. Among the 12 modes with even parity, the  $A_g + E_g + 3T_g$  modes all correspond to rotationally related modes.

In the case of  $^{12}\text{C}_{60}$ , Raman-active librations in a crystal with  $T_h$  group symmetry include only modes with  $A_g$  symmetry among the 24 intermolecular modes [see Eq. (3)]. Thus the probability for finding the  $\Gamma$  irreducible representation is unity for  $\Gamma = A_g$  states and zero for other irreducible representations.

In the case of  $^{13}\text{C}_{60}$ , we see below that the symmetry of the nuclear spin states makes all librational modes allowed. The Raman-active librational mode should satisfy the condition

$$\Psi_{\text{lib}} \Psi_{\text{ns}} \rightarrow A_g, E_g, T_g$$

since all even-parity symmetry types for  $T_h$  symmetry occur for the librational modes. If the direct product of the irreducible representation for  $\Psi_{\text{lib}}$  with that for  $\Psi_{\text{ns}}$  has even parity, then the corresponding librational mode is Raman allowed.

For  $^{13}\text{C}_{60}$ , the probability that  $\Psi_{\text{ns}}$  transforms according to the irreducible representation  $\Gamma$  is given in Table VII. These probabilities are obtained by the reduction of the irreducible representations of the high symmetry  $I_h$  group (Table II) to those of the lower symmetry  $T_h$  group (see Table VIII). For example, the  $E_g$  state of the  $T_h$  group comes only from the  $H_g$  states of  $I_h$  [ $H_g(I_h) \rightarrow T_g(T_h) + E_g(T_h)$ ] while  $A_g(T_h)$  comes only from  $A(I_h)$  and  $G(I_h)$ . From Table VII it is seen that the probability of nuclear spin states having even and odd parity is 1/2 and 1/2, respectively, and the librational modes include all the irreducible representations of group  $T_h$ , i.e.,  $A_g$ ,  $E_g$ ,  $T_g$ ,  $A_u$ ,  $E_u$ , and  $T_u$  (see Table VII).

We note that there is a large difference between the allowed librational motions in the  $^{12}\text{C}_{60}$  solid, which allows only  $A_g$  librations, and the  $^{13}\text{C}_{60}$  solid, which allows all librations according to the probabilities given in Table VII. These probabilities are obtained by the reduction of the irreducible representations of the high symmetry  $I_h$  group (Table II) to those of the lower symmetry  $T_h$  group (Table VIII).

In the absence of librations, the vibrational modes of the solid state are also restricted, but in different ways for  $^{12}\text{C}_{60}$  and  $^{13}\text{C}_{60}$ . The number of vibrational modes in solid  $\text{C}_{60}$  is given in Table IX.<sup>12</sup> In the case of  $^{12}\text{C}_{60}$ , only vibrational modes with  $A_g$  symmetry are Pauli allowed. In contrast, for  $^{13}\text{C}_{60}$ , each vibrational mode can be partially allowed with a probability determined by the nuclear spin states listed in Table X. For example, the  $T_g$  vibration is possible only when the nuclear spin state has  $T_g$  symmetry, which occurs with a probability of 3/10 (Table VII). Since  $T_g \otimes T_g = 2T_g + A_g + E_g$ , the probability of finding  $A_g$  symmetry in the direct product is only 1/9.

TABLE VII. Probability of nuclear spin states of the molecule  $^{13}\text{C}_{60}$  in  $T_h$  symmetry.

$\mathcal{I}(^{13}\text{C}_{60})$	$A_g$	:	$E_g$	:	$T_g$	:	$A_u$	:	$E_u$	:	$T_u$
	1/10	:	1/10	:	3/10	:	1/10	:	1/10	:	3/10

TABLE VIII. Symmetry lowering and compatibility relations between several point groups.

$I_h$	$I$	$T_h$	$D_{5d}$	$D_5$	$C_\sigma$
$A_g$	$A$	$A_g$	$A_{1g}$	$A_1$	$A_1$
$F_{1g}$	$F_1$	$T_g$	$A_{2g} + E_{1g}$	$A_2 + E_1$	$A_1 + 2A_2$
$F_{2g}$	$F_2$	$T_g$	$A_{2g} + E_{2g}$	$A_2 + E_2$	$A_1 + 2A_2$
$G_g$	$G$	$A_g + T_g$	$E_{1g} + E_{2g}$	$E_1 + E_2$	$2A_1 + 2A_2$
$H_g$	$H$	$E_g + T_g$	$A_{1g} + E_{1g} + E_{2g}$	$A_1 + E_1 + E_2$	$3A_1 + 2A_2$
$A_u$	$A$	$A_u$	$A_u$	$A_1$	$A_2$
$F_{1u}$	$F_1$	$T_u$	$A_{2u} + E_{1u}$	$A_2 + E_1$	$2A_1 + A_2$
$F_{2u}$	$F_2$	$T_u$	$A_{2u} + E_{2u}$	$A_2 + E_2$	$2A_1 + A_2$
$G_u$	$G$	$A_u + T_u$	$E_{1u} + E_{2u}$	$E_1 + E_2$	$2A_1 + 2A_2$
$H_u$	$H$	$E_u + T_u$	$A_{1u} + E_{1u} + E_{2u}$	$A_1 + E_1 + E_2$	$3A_1 + 2A_2$

TABLE IX. The number of vibrational modes for each irreducible representation in solid  $\text{C}_{60}$  for various space group symmetries. (Note the two different lines with regard to the  $g$  and  $u$  modes.)

Vibrational mode	$A_g$	$E_g$	$T_g$	$A_u$	$E_u$	$T_u$
$T_h, T_h^5$ ( $\text{M}_6\text{C}_{60}$ solid)	8	8	21	7	7	22
$T_h^6$ ( $\text{C}_{60}$ solid)	29	29	87	29	29	87

TABLE X. Probabilities for each type of vibration in  $^{13}\text{C}_{60}$  (solid), expressed in terms of symmetries of point group  $T_h$ .

Vibration	$A_g$	$E_g$	$T_g$	$A_u$	$E_u$	$T_u$
$T_h, T_h^5, T_h^6$	1/10	1/20	1/30	1/10	1/20	1/30

TABLE XI. The character table of  $C_\sigma$ 

$C_\sigma$	$E$	$\sigma$	Basis functions
$A_1$	1	1	$x, y, x^2, y^2, z^2, xy$
$A_2$	1	-1	$z, xz, yz$

TABLE XII. Decomposition of irreducible representations of  $I_h$  to those of  $C_\sigma$ .

$A_g$	$\rightarrow$	$A_1$	$A_u$	$\rightarrow$	$A_2$
$F_{1g}, F_{2g}$	$\rightarrow$	$A_1 + 2A_2$	$F_{1u}, F_{2u}$	$\rightarrow$	$2A_1 + A_2$
$G_g$	$\rightarrow$	$2A_1 + 2A_2$	$G_u$	$\rightarrow$	$2A_1 + 2A_2$
$H_g$	$\rightarrow$	$3A_1 + 2A_2$	$H_u$	$\rightarrow$	$2A_1 + 3A_2$

TABLE XIII. Decomposition of irreducible representations of  $T_h$  to those of  $C_\sigma$ .

$A_g$	$\rightarrow$	$A_1$	$A_u$	$\rightarrow$	$A_2$
$E_g$	$\rightarrow$	$2A_1$	$E_u$	$\rightarrow$	$2A_2$
$T_g$	$\rightarrow$	$A_1 + 2A_2$	$T_u$	$\rightarrow$	$2A_1 + A_2$

Thus the total probability that the  $^{13}\text{C}_{60}$  solid is set into a vibration with  $T_g$  symmetry is  $(3/10) \times (1/9) = 1/30$ . Although all modes are symmetry allowed, the intensity of certain symmetry modes becomes small because of symmetry restrictions associated with the nuclear spin states.

#### D. Lower symmetry cases

Finally, we consider molecules with lower symmetry. With a natural abundance of  $^{13}\text{C}$  (1.1%), the probabilities for occurrence of the  $^{12}\text{C}_{60}$ ,  $^{13}\text{C}_1^{12}\text{C}_{59}$ ,  $^{13}\text{C}_2^{12}\text{C}_{58}$ , and  $^{13}\text{C}_3^{12}\text{C}_{57}$  molecules are 51.2%, 34.5%, 11.4%, and 2.5%, respectively. The probability of isomer molecules with four or more  $^{13}\text{C}$  atoms per fullerene has a probability of less than 0.5%. Although it is possible to discuss the statistics of a  $^{13}\text{C}_x^{12}\text{C}_{60-x}$  molecule in the unit cell of the solid generally, we here consider only the cases of  $^{13}\text{C}_1^{12}\text{C}_{59}$  and  $^{13}\text{C}_2^{12}\text{C}_{58}$ . A mixture of the various isotopically distributed molecules results in no point-group symmetry in most cases and thus there will no longer be any symmetry restrictions associated with nuclear spin states.

In the case of the  $^{13}\text{C}_1^{12}\text{C}_{59}$  molecule, the symmetry is drastically changed from the high symmetry point group  $I_h$  to the low symmetry  $C_\sigma$  point group (see Table VIII). In the  $C_\sigma$  point group there are only  $E$  and  $\sigma$  symmetry operations in which the mirror plane  $\sigma$  passes through the  $^{13}\text{C}$  atom. The character table and basis functions for each irreducible representation of  $C_\sigma$  are shown in Table XI. For group  $C_\sigma$ , all electronic, vibrational, and rotational states are nondegenerate. Since nuclear states with  $\mathcal{I} = 1/2$  change sign by the  $\sigma$  operation,  $\Psi_{ns}$  transforms according to the irreducible representation  $A_2$ . The  $A_1$  and  $A_2$  vibrations are both infrared active and Raman active. The decomposition of the irreducible representations of  $I_h$  into those of  $C_\sigma$  is given in Table XII and the decomposition of the irreducible representations of  $T_h$  into those of  $C_\sigma$  is given in Table XIII.

In the free rotation of a  $^{13}\text{C}_1^{12}\text{C}_{59}$  molecule,  $\Psi_{rot}$  transforms according to  $A_2$ . Thus the  $J = 0$  rotational state is not allowed, but the  $J = 1$  state is allowed with a probability of  $1/3$ . At a high temperature for the rotational modes, the ratio of the  $A_1$  and  $A_2$  states in the rotational modes may approach 1:1. Thus vibration-rotation coupling of a  $^{13}\text{C}_1^{12}\text{C}_{59}$  molecule leads to having all vibrational states appear with the same probability of  $1/2$ . In a similar way, all librational motion and all vibrational modes in the solid are allowed with a probability of  $1/2$ .

In the case of the  $^{13}\text{C}_2^{12}\text{C}_{58}$  molecule, there are three possible lower symmetry groups:  $C_1$ ,  $C_\sigma$ , and  $C_{2v}$  with probabilities  $56/59$ ,  $1/59$ , and  $2/59$ , respectively. In the case of  $C_1$  symmetry, there are no symmetry restrictions and all vibrational and rotational modes of the molecule or of the solid appear with an equal probability of unity, and the mode intensities reflect only the icosahedral  $I_h$  symmetry.

For  $^{13}\text{C}_2^{12}\text{C}_{58}$  the nuclear spin states have either  $\mathcal{I} = 1$  or  $\mathcal{I} = 0$ , which are even and odd with regard to mirror symmetry, with a probability ratio of 3:1. This weighting

effect might be observable for the free molecule, but in the solid state it would be difficult to observe such restricted motion, because of its low probability.

### III. ISOTOPE EFFECTS ON PHYSICAL PROPERTIES

In this section we list several possible experiments which may show isotope effects for the various physical properties of  $^{12}\text{C}_{60}$ ,  $^{13}\text{C}_{60}$ , and other isotopic molecular combinations. Among these, pure  $^{12}\text{C}_{60}$  is the most symmetrical molecule since there are no nuclear spin states. Thus experiments on pure  $^{12}\text{C}_{60}$  would be most desirable for showing symmetry effects most clearly. To have  $^{12}\text{C}_{60}$ , no atom in the  $\text{C}_{60}$  molecule can be  $^{13}\text{C}$ , so that very high isotopic purity is necessary. When one uses 99.9%, 99.99%, or 99.999% purified  $^{12}\text{C}$  atoms, the purity of  $^{12}\text{C}_{60}$  becomes 94.1%, 99.4%, or 99.9%, respectively.

In Raman spectroscopy experiments of pure  $^{12}\text{C}_{60}$  at very low temperature ( $T < 1$  K), no rotational or librational modes would be expected. In this case  $H_g$ -derived Raman-active modes are strongly suppressed because of symmetry restrictions. If we use 5%  $^{13}\text{C}$  enriched carbon for making  $\text{C}_{60}$ , 95% of  $\text{C}_{60}$  molecules have no symmetry regarding their vibrational modes and thus we expect that many Raman-active modes will become observable, though their intensities may not be so strong because of the weak broadening of the vibrational spectra. If a special technique could be devised that could select only  $^{13}\text{C}^{12}\text{C}_{59}$  molecules, many interesting properties could also become observable.

The specific heat measurement at low temperature (below 5 K) would be very different in the case of  $^{12}\text{C}_{60}$  since the acoustic branch of the phonon modes has odd parity, and thus to obtain even-parity phonons we need to excite an even number of phonons for a particular acoustic branch. This effect is further discussed below.

The first-order phase transition at 261 K (Ref. 16) has been identified as the transition from a low temperature ratchet-motion phase to a free rotational phase. Many experimental techniques such as specific heat, NMR, and inelastic neutron scattering measurements clearly show this phase transition.<sup>16</sup> Theoretical calculations of the specific heat using the density of states for the 24 librational and intermolecular vibrational modes<sup>17</sup> reproduce the experimental specific heat very well, except for the excess heat appearing below the critical temperature. The specific heat experiment also shows an excess enthalpy of  $30 \text{ J K}^{-1} \text{ mol}^{-1}$ , which can be estimated by considering the orientational disorder as follows. Theoretical molecular dynamics experiments and x-ray diffraction experiments, at a temperature lower than the glassy phase transition at 86.8 K, show that the direction of the 30 double bonds  $\text{C}=\text{C}$  for a  $\text{C}_{60}$  molecule may be in a potential minimum regarding the ratchet motion. Physically the potential minimum is associated with placement of the electron rich  $\text{C}=\text{C}$  double bonds on one molecule close to the center of the electron-poor pentagonal faces of the adjacent molecule. The entropy change corresponding to the alignment of  $N$  molecules, which initially have a

random orientation, into an ordered phase is

$$\Delta S = k_B \ln(30)^N = 28.3 \text{ J K}^{-1} \text{ mol}^{-1}, \quad (4)$$

which is very close to the experimental value of  $30 \text{ J K}^{-1} \text{ mol}^{-1}$ . Here we use the value  $N = 6.02 \times 10^{23}$  for Avogadro's number. The difference  $\Delta S$  arises from the additional ratcheting between states that become coupled to the nuclear spin states due to the existence of a natural abundance of  $^{13}\text{C}$  isotopes in the  $\text{C}_{60}$  molecules. A phase transition thus occurs as a result of the competition between the enthalpy loss in the low temperature simple cubic structure relative to the face-centered-cubic phase, and the entropy gain associated with the transition from the ratchet motion to free rotation.

In the case of pure  $^{12}\text{C}_{60}$ , the value of the entropy will approach the value given in Eq. (4). Because of the relatively small persistence of disorder in the case of  $^{12}\text{C}_{60}$ , the transition temperature  $T_c$  for the pure  $^{12}\text{C}_{60}$  solid is expected to increase relative to that of  $\text{C}_{60}$  made from carbon atoms with the natural isotopic abundance. On the other hand, the  $^{13}\text{C}$ -enriched  $\text{C}_{60}$  (enriched, for example, to 5%) will have a lower transition temperature because of the increased isotopic disorder. In the case of the pure  $^{13}\text{C}_{60}$  molecule, since the symmetry again becomes higher relative to the natural abundance, the critical temperature will increase again, but the critical temperature should not be as high as that for pure  $^{12}\text{C}_{60}$  because of the larger number of nuclear spin states and the larger value of momentum of inertia for the case of  $^{13}\text{C}_{60}$ .

### IV. CONCLUSION

In conclusion, we have discussed symmetry-restricted rotations and vibrations of  $^{12}\text{C}_{60}$  and  $^{13}\text{C}_{60}$  and have illustrated the general discussion with a number of examples. The probability for excitation of vibrations and rotations is calculated for free molecular motion in vacuum and for librational motion in the solid. It is especially important to use pure  $^{12}\text{C}_{60}$  samples for the most dramatic demonstration of the statistical effects described in this paper.

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### APPENDIX: DECOMPOSITION OF THE $I = 1/2$ SPIN SYSTEM

In this Appendix we calculate the decomposition of the  $N = 60$ ,  $I = 1/2$  spin system into the irreducible

TABLE XIV. Reducible characters for the subspace of  $\{\mathcal{I}_{\text{tot}} = m\}$ .

$\mathcal{I}_z$	$E$	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$	$i$	$12iC_5$	$12iC_5^2$	$20iC_3$	$15iC_2$
30	1	1	1	1	1	1	1	1	1	1
29	60	0	0	0	0	0	0	0	0	4
28	1770	0	0	0	30	30	0	0	0	34

representations of  $I_h$ . All operations of  $I_h$  which permute with the atomic sites of the nuclear spins can be expressed by permutations of 60 elements. First let us consider the subspace of  $\{\mathcal{I}_z = m, (m = -30, \dots, 30)\}$ . The number of up and down spins  $n_\uparrow$  and  $n_\downarrow$  are

$$n_\uparrow = \frac{N}{2} + m, \quad n_\downarrow = \frac{N}{2} - m. \quad (\text{A1})$$

The dimension  $d_m$  of the subspace  $\{\mathcal{I}_z = m\}$ , is given by the binomial factor

$$d_m = \frac{N!}{n_\uparrow!n_\downarrow!}. \quad (\text{A2})$$

The basis function of the subspace is expressed by

$$\phi_i = \alpha_1\alpha_2\alpha_3 \cdots \alpha_{60} \quad (i = 1, \dots, d_m) \quad (\text{A3})$$

in which  $\alpha_j$  denotes the  $j$ th spin and the number of  $\alpha$  (spin  $\uparrow$ ) and  $\beta$  (spin  $\downarrow$ ) is given by Eq. (A1).

Next we consider the subspace  $\{\mathcal{I}_{\text{tot}} = m\}$  in which the magnitude of the total spin is constant. It is easy to show that the dimension  $D_m$  of the subspace  $\{\mathcal{I}_{\text{tot}} = m\}$  is given by

$$D_m = d_m - d_{m+1}, \quad (\text{A4})$$

since all functions of  $\{\mathcal{I}_z = m+1\}$  form a one-to-one correspondence to those of  $\{\mathcal{I}_z = m\}$  by the  $S^-$  operation. Since  $S^\pm$  commutes with all permutations, all functions of  $\{\mathcal{I}_z = m+1\}$  transform as irreducible representations, which have a one-to-one correspondence to those in the same irreducible representation of  $\{\mathcal{I}_z = m\}$ . From this fact, we can show that

$$D_m^\Gamma = d_m^\Gamma - d_{m+1}^\Gamma, \quad (\text{A5})$$

where  $D_m^\Gamma$  and  $d_m^\Gamma$  are the dimensions of  $\{\mathcal{I}_{\text{tot}} = m\}$  and of  $\{\mathcal{I}_z = m\}$  in the  $\Gamma$  irreducible representation of  $I_h$ .

From Eq. (A5) we can calculate the decomposition of the space of  $\{\mathcal{I}_{\text{tot}} = m\}$  into the irreducible representations of  $I_h$  by calculating the reducible characters of the space of  $\{\mathcal{I}_z = m\}$ . For any operation  $R$  of  $I_h$  expressed by a permutation of 60 elements, a basis function of Eq. (A3) is transformed into other basis functions, that is,

$$R\phi_i = \phi_j. \quad (\text{A6})$$

Thus the reducible characters for an operation  $R$  are given by the number of cases for which  $\phi_i = \phi_j$ . Since all operations of  $I_h$  except for  $E$  and  $\sigma$  change all atomic sites, the spin directions in a cyclic permutation appearing in operation  $R$  should be preserved to yield the condition of  $\phi_i = \phi_j$ .

The classes  $I_h$ ,  $E$ ,  $C_5$ ,  $C_5^2$ ,  $C_3$ ,  $C_2$ ,  $i$ ,  $iC_5$ , etc. are expressed, respectively, by a set of cyclic permutation as

$\{1^{60}\}$ ,  $\{5^{12}\}$ ,  $\{5^{12}\}$ ,  $\{3^{20}\}$ ,  $\{2^{30}\}$ ,  $\{2^{30}\}$ ,  $\{10^6\}$ , etc. Special care must be taken in writing down the permutations equivalent to  $\sigma = iC_2$ , since there are four atomic invariant sites which are spanned by  $\sigma$ .

The reducible characters are easily obtained as follows:

$$\begin{aligned} \chi(E) &= \frac{N!}{n_\uparrow!n_\downarrow!}, \\ \chi(C_5) &= \begin{cases} \frac{(\frac{N}{5})!}{(\frac{n_\uparrow}{5})!(\frac{n_\downarrow}{5})!} & \text{if } n_\uparrow \bmod 5 = 0 \\ 0 & \text{otherwise,} \end{cases} \\ \chi(C_5^2) &= \begin{cases} \frac{(\frac{N}{5})!}{(\frac{n_\uparrow}{5})!(\frac{n_\downarrow}{5})!} & \text{if } n_\uparrow \bmod 5 = 0 \\ 0 & \text{otherwise,} \end{cases} \\ \chi(C_3) &= \begin{cases} \frac{(\frac{N}{3})!}{(\frac{n_\uparrow}{3})!(\frac{n_\downarrow}{3})!} & \text{if } n_\uparrow \bmod 3 = 0 \\ 0 & \text{otherwise,} \end{cases} \\ \chi(C_2) &= \begin{cases} \frac{(\frac{N}{2})!}{(\frac{n_\uparrow}{2})!(\frac{n_\downarrow}{2})!} & \text{if } n_\uparrow \bmod 2 = 0 \\ 0 & \text{otherwise,} \end{cases} \\ \chi(i) &= \begin{cases} \frac{(\frac{N}{2})!}{(\frac{n_\uparrow}{2})!(\frac{n_\downarrow}{2})!} & \text{if } n_\uparrow \bmod 2 = 0 \\ 0 & \text{otherwise,} \end{cases} \\ \chi(iC_5) &= \begin{cases} \frac{(\frac{N}{10})!}{(\frac{n_\uparrow}{10})!(\frac{n_\downarrow}{10})!} & \text{if } n_\uparrow \bmod 10 = 0 \\ 0 & \text{otherwise,} \end{cases} \\ \chi(iC_5^2) &= \begin{cases} \frac{(\frac{N}{10})!}{(\frac{n_\uparrow}{10})!(\frac{n_\downarrow}{10})!} & \text{if } n_\uparrow \bmod 10 = 0 \\ 0 & \text{otherwise,} \end{cases} \\ \chi(iC_3) &= \begin{cases} \frac{(\frac{N}{6})!}{(\frac{n_\uparrow}{6})!(\frac{n_\downarrow}{6})!} & \text{if } n_\uparrow \bmod 6 = 0 \\ 0 & \text{otherwise,} \end{cases} \\ \chi(\sigma) &= \begin{cases} \frac{29! \cdot 4}{(\frac{n_\uparrow-1}{2})!(\frac{n_\downarrow-1}{2})!} & \text{if } n_\uparrow \bmod 2 = 1 \text{ and } n_\uparrow \geq 3 \\ \frac{28! \cdot (870 + n_\uparrow n_\downarrow)}{(\frac{n_\uparrow}{2})!(\frac{n_\downarrow}{2})!} & \text{if } n_\uparrow \bmod 2 = 0 \text{ and } n_\uparrow \geq 4 \\ 1 & \text{if } n_\uparrow = 0 \\ 4 & \text{if } n_\uparrow = 1 \\ 34 & \text{if } n_\uparrow = 2. \end{cases} \end{aligned} \quad (\text{A7})$$

TABLE XV. Decomposition of the space of  $\{\mathcal{I}_{\text{tot}} = m\}$  to  $I_h$  irreducible representations.

$m$	$A_g$	$F_{1g}$	$F_{2g}$	$G_g$	$H_g$	$A_u$	$F_{1u}$	$F_{2u}$	$G_u$	$H_u$
30	1	0	0	0	0	0	0	0	0	0
29	0	1	1	2	3	0	2	2	2	2
28	22	36	36	58	80	14	42	42	56	70



Here  $\chi(\sigma)$  takes on special values 1, 4, and 34 for  $n_{\uparrow}=0, 1,$  and  $2,$  respectively. The calculated reducible characters for the subspace  $\{\mathcal{I}_{\text{tot}} = m\}$  are given in Table XIV, in which we show results only for  $\mathcal{I}_z = 28, 29,$  and  $30$  for simplicity. Using the relationship of Eq. (A5), we obtain the final decomposition of the space of  $\{\mathcal{I}_{\text{tot}} = m\}$  as

given in Table XV.

The numbers of states in an irreducible representation for smaller values of  $\mathcal{I}$  increases rapidly with increasing  $\mathcal{I}$ . However, it is not difficult to calculate them using appropriate software for analytic calculations, such as MAPLE at Athena, MIT.

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