

Force-constant model for the vibrational modes in C_{70}

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A force-constant model previously developed for C_{60} is extended to C_{70} . Using the force constants determined for the C_{60} molecule, the vibrational frequencies for the C_{70} molecule are calculated and are identified with the irreducible representations of the D_{5h} symmetry group, according to which the vibrational modes transform. A comparison of the predictions of this model with the experimentally reported values for the Raman- and infrared-active modes shows good agreement overall. The effect of doping by alkali-metal atoms is taken into account by modifying the force constants in order to produce a good fit to the available data for doped C_{60} . The model is then used to predict the frequencies of the Raman- and infrared-active modes in alkali-metal-doped C_{70} .

I. INTRODUCTION

In the production of C_{60} by laser evaporation¹ or electrical arc discharge² of graphite, appreciable amounts of other fullerenes, particularly C_{70} , are produced. The C_{70} molecule is ellipsoidal in shape and has the symmetry group D_{5h} .^{3,4} This structure lacks inversion symmetry, but has mirror symmetry instead. Nuclear magnetic resonance (NMR) measurements are consistent with the ellipsoidal structure, showing a NMR spectrum with five resonant lines, in contrast to C_{60} which shows a single NMR line.⁵ In addition to the two nearly hemispherical caps that form the icosahedral C_{60} molecule, the C_{70} molecule contains a belt of ten additional carbon atoms located in five hexagons along the equator of the ellipsoid, perpendicular to a fivefold symmetry axis.

The vibrational frequencies of C_{60} and C_{70} have been measured by a variety of techniques. Raman scattering (RS),⁶⁻⁸ infrared absorption (IR),⁷⁻¹¹ inelastic neutron scattering (NIS),^{12,13} high-resolution electron-energy-loss (HREELS) spectroscopy,¹⁴ and photoluminescence¹⁵ have been employed in the study of the vibrational modes in C_{60} , and taken together, they provide a comprehensive picture of the vibrational modes of C_{60} . Consistent with the more limited availability of pure C_{70} , the experimental data for vibrational modes in C_{70} are much

more limited, with only Raman scattering and infrared absorption measurements reported so far.^{8,9,16}

Several calculations of the frequencies of the vibrational modes of the C_{60} molecule were performed using various theoretical approaches: modified neglect of differential overlap (MNDO),¹⁷ quantum consistent force field for π electrons (QCFF/PI),¹⁸ self-consistent-field treatment using Slater-type orbitals with three Gaussians (STO-3G/SCF),¹⁹ double- ζ polarization with Moller-Plesset second-order perturbation (DZP/MP2),²⁰ real space quantum molecular dynamics (QMD),²¹ and Car-Parinello molecular dynamics.²² Of these, the QCFF/PI method,¹⁸ which has been parametrized with respect to the vibrational frequencies of conjugated and aromatic hydrocarbons,²³ gives the best results for the vibrational frequencies in C_{60} . In addition, there have been a number of force-constant models employed to calculate the vibrational frequencies for the C_{60} molecule.²⁴⁻²⁶ When the force-constant model for C_{60} is framed to include interactions through third nearest neighbors, and including four bond-stretching and four angle-bending force constants, good agreement with the experimental vibrational frequencies is obtained for the various mode frequencies that have been measured to date.²⁷

For the C_{70} molecule, fewer calculations of the vibrational frequencies have been reported in the literature.

Assuming a structure with D_{5h} symmetry, Slanina *et al.*²⁸ calculated the vibrational frequencies of C_{70} using the Austin model 1 (AM1) technique. Comparison of these calculations to the observed Raman-active modes was not possible because the irreducible representations, according to which the vibrational modes transform, were not determined. As for the infrared-active modes, no obvious correspondence between the patterns of the calculated and observed⁸ spectra could be discerned.

More recently, the vibrational frequencies of C_{70} were calculated at the MNDO level.²⁹ Only the frequencies of the IR-active modes and the completely symmetric non-degenerate Raman-active modes were reported. Similar to the case in C_{60} , the frequencies of the high-frequency tangential modes in C_{70} calculated by the MNDO technique are ~ 200 cm^{-1} higher than the measured values. Similar results were obtained for the vibrational frequencies in C_{60} and C_{70} by use of tight-binding molecular dynamics.³⁰ Better agreement with experiment was obtained by the use of the QCFF/PI method,³¹ and a complete listing of the eigenfrequencies and their symmetries was obtained. However, no attempt was made in that work to compare in detail the observed Raman- and infrared-active modes with the results of the calculation. A force-constant model using a Born potential was reported recently³² but a comparison between the calculated and measured frequencies shows poor agreement.

In the present work, we extend a force-constant model for C_{60} which includes atom-atom interactions up to the third-nearest neighbors,²⁷ to yield information about the vibrational modes for C_{70} . The force constants used in the model for C_{60} (Ref. 27) were introduced under the following assumptions. Each atom is assumed to be a point mass and to be connected by springs to its first-, second-, and third-nearest neighbors. Two springs, with spring constants s_p and s_h , are used to model the stretching of the pentagonal and hexagonal bonds, respectively. The stretching of bonds connecting an atom to its second-nearest neighbors, whether these bonds lie in the pentagonal or hexagonal faces, is modeled by springs with spring constant s_2 . A bond connecting an atom to its third-nearest neighbor will lie in a hexagonal face only, and the corresponding spring constant is s_3 . The bending of the pentagonal angle of 108° and the hexagonal angle of 120° is modeled by torsional springs with spring constants a_p and a_h , respectively (see Table I). In addition, the bending of the angles between the spring connecting an atom to its first-nearest neighbors and the springs connecting this atom to its second- and third-nearest neighbors are modeled by springs of spring constants b and c , respectively. The eigenfrequencies obtained with this model were shown to be in excellent agreement with all the experimental data obtained by Raman scattering, infrared, inelastic neutron, and high-resolution energy-loss spectroscopies.²⁷

It is the purpose of this paper to apply this force-constant model, originally developed for C_{60} to the calculation of the frequencies of the vibrational modes in C_{70} , to classify the modes according to the irreducible representations of the symmetry group for C_{70} , and to compare the predictions of this model to available ex-

TABLE I. The values of the bond-stretching force constants (K_{str}), in $\text{mdyn}/\text{\AA}$, and of the angle-bending force constants (K_{bend}), in $\text{mdyn \AA}/(\text{rad})^2$, used in the force-constant model for the vibrational modes in C_{60} and C_{70} . The primed quantities are the corresponding values used in M_6C_{60} and M_6C_{70} .

K_{str}	Value	K_{bend}	Value
s_p	2.35	a_p	1.0
s_h	4.0	a_h	0.25
s_2	1.21	b	0.095
s_3	-1.05	c	0.325
s'_p	2.6	a'_p	0.8
s'_h	3.4	a'_h	0.2
s'_2	1.2	b'	0.077
s'_3	-0.85	c'	0.26

perimental data. As a zeroth-order approximation, the same set of force constants as was used in the case of C_{60} is now used to calculate the eigenfrequencies in C_{70} . A perturbation whose effect is to reduce the shear forces between the belt atoms and the atoms in the adjacent layers is then introduced and is shown to lead to an improved set of calculated eigenfrequencies, while introducing only two additional parameters.

In addition, we consider how the force constants in C_{60} are modified by doping with alkali-metal atoms, using exactly the same functional form of the dynamical matrix as was used for the case of undoped C_{60} . The modified force constants are then used to predict the frequencies of the Raman-active and infrared-active modes in the alkali-metal-doped C_{70} . Insofar as the vibrational frequencies for alkali-metal-doped C_{70} have not yet been reported, this calculation should be useful for experimentalists embarking on measurements of the vibrational spectra in doped C_{70} . The approach taken here can further be extended to obtain approximate descriptions for phonon modes in yet larger fullerenes.

II. VIBRATIONAL MODES IN C_{70}

The structure of the C_{70} molecule has D_{5h} as its symmetry group. The character table for the point group D_{5h} , along with the basis functions that transform according to the various irreducible representations, is presented in Table II. By decomposing the $(210-6=204)$ -dimensional reducible representation according to which the coordinates of the 70 carbon atoms of C_{70} transform, the number of distinct eigenvalues, corresponding to vibrational modes that transform according to each irreducible representation of the point group D_{5h} , can be determined. There are 122 distinct nonzero vibrational frequencies which result from diagonalizing the dynamical matrix. In Table III the irreducible representations of point group D_{5h} are listed together with the number of distinct eigenvalues N_ω and the corresponding degeneracies g for each irreducible representation of D_{5h} . The cap and belt modes (N_ω^{cap} and N_ω^{belt}), which are more clearly delineated below, are also listed separately. In the listings of this table, the six degrees of freedom corresponding to pure translations and rotations of the molecule have al-

TABLE II. Character table for the point group D_{5h} . Note that $\tau = (1 + \sqrt{5})/2$ so that $\tau = -2 \cos(2\alpha) = -2 \cos(4\pi/5)$ and $\tau - 1 = 2 \cos \alpha = 2 \cos(2\pi/5)$. Modes with $A'_1, E'_2,$ and E''_1 symmetries are Raman active, while modes with E'_1 and A'_2 symmetries are infrared active.

D_{5h}	E	$2C_5$	$2C_5^2$	$5C_2'$	σ_h	$2S_5$	$2S_5^3$	$5\sigma_v$	Basis functions
A'_1	+1	+1	+1	+1	+1	+1	+1	+1	$x^2 + y^2, z^2$
A'_2	+1	+1	+1	-1	+1	+1	+1	-1	R_z
E'_1	+2	$\tau - 1$	$-\tau$	0	+2	$\tau - 1$	$-\tau$	0	$(x, y), (xz^2, yz^2), [x(x^2 + y^2), y(x^2 + y^2)]$
E'_2	+2	$-\tau$	$\tau - 1$	0	+2	$-\tau$	$\tau - 1$	0	$(x^2 - y^2, xy), [y(3x^2 - y^2), x(x^2 - 3y^2)]$
A''_1	+1	+1	+1	+1	-1	-1	-1	-1	
A''_2	+1	+1	+1	-1	-1	-1	-1	+1	$z, z^3, z(x^2 + y^2)$
E''_1	+2	$\tau - 1$	$-\tau$	0	-2	$1 - \tau$	$+\tau$	0	$(R_x, R_y), (xz, yz)$
E''_2	+2	$-\tau$	$\tau - 1$	0	-2	$+\tau$	$1 - \tau$	0	$[xyz, z(x^2 - y^2)]$

ready been subtracted, leaving a total of 204 vibrational degrees of freedom for the dynamical matrix. The symmetries of the belt modes are found by forming the direct product of the equivalence transformation $\chi^{\text{atom sites}}$ for the belt atoms with the irreducible representations of the vector. The symmetries of the cap modes of C_{70} are then found by subtraction of N_{ω}^{belt} from the total N_{ω} for the C_{70} molecule.

We have carried out a calculation of the frequencies and corresponding eigenvectors of the vibrational modes in the C_{70} molecule using the force-constant model discussed above, incorporating the lower D_{5h} symmetry of the C_{70} molecule into the calculation. The values of the force-constant parameters used in the lowest-order calculation of the vibrational modes in C_{70} are given in Table I, and are the same values as were used in the calculation of the mode frequencies in C_{60} .²⁷ These force constants were determined by fitting the calculated frequencies for the Raman-active modes to the measured Raman frequencies for C_{60} .

The equivalence of all the atomic sites in C_{60} implies that there are only two different bond lengths connecting nearest-neighbor carbon atoms, and two different angles between such bonds. For the nearest-neighbor interactions in C_{60} , two bond-stretching force constants, s_p and s_h , for the pentagonal and hexagonal bonds, respectively, are assumed, as well as two angle-bending force constants, a_p and a_h , for the pentagonal and hexagonal angles, respectively.

TABLE III. The D_{5h} irreducible representations (\mathcal{R}) together with the number of distinct eigenvalues (N_{ω}) and the corresponding degeneracies g . The symbols N_{ω}^{belt} and N_{ω}^{cap} denote the number of distinct eigenvalues associated with the "belt" and "cap" modes, respectively, for each irreducible representation.

\mathcal{R}	N_{ω}^{belt}	N_{ω}^{cap}	N_{ω}	g
A'_1	2	10	12	1
A'_2	2	7	9	1
E'_1	4	17	21	2
E'_2	4	18	22	2
A''_1	1	8	9	1
A''_2	1	9	10	1
E''_1	2	17	19	2
E''_2	2	18	20	2

The lower D_{5h} symmetry for the C_{70} molecule implies that there are five inequivalent atomic sites in the C_{70} molecule, which, in turn, allows for the existence of eight different bond lengths as well as 12 different angles between the bonds connecting nearest-neighbor atoms.²⁹ Thus if only nearest-neighbor interactions are considered in constructing the dynamical matrix, the lower symmetry of the C_{70} molecule requires consideration of eight different bond-stretching and 12 different angle-bending force constants. In the lowest-order model, we have considered only two distinct bond-stretching and two distinct angle-bending force constants for bonds connecting nearest-neighbor atoms. In this approximation, each bond is classified as either long or short, depending on whether its length is longer or shorter than the average bond length. Similarly, an angle is classified as either belonging to a pentagon or a hexagon. Although this lowest-order approximation for C_{70} is certainly an oversimplification of the C_{70} structure, nevertheless, we feel that this model contains the basic physics, has no adjustable parameters, and provides a first-order approximation to the molecular vibrations for C_{70} . A comparison of the calculated mode frequencies to the experimental data for C_{70} , presented below, shows that this crude approximation can account for most of the experimental observations.

The determination of the irreducible representations according to which the various modes transform can be achieved once the eigenvectors are determined. For non-degenerate modes, the irreducible representations can be determined by inspecting the transformation properties of the eigenvectors under horizontal and vertical reflection planes. For twofold degenerate modes, inspection of the effect of the reflection in the horizontal plane as well as the rotation about the fivefold axis on the eigenvectors is carried out in making the symmetry identification.

The values of the 122 distinct vibrational frequencies for the C_{70} molecule calculated in this simple way are given in Table IV, along with the irreducible representation labels of the corresponding modes. In this table we also give the percent radial character of the atomic displacements P_r for each of the 122 modes. Values for P_r are obtained by considering the ratio of the sum of the squares of the radial components of the atomic displacement vectors to the sum of the squares of all the displacement vectors for mode ω . It is of interest to

TABLE IV. All calculated modes for C₇₀ using the same set of force constants as in C₆₀. The frequencies ω are expressed in cm⁻¹ while P_r and P_b denote percentages of the radial and belt character of each mode.

Modes (in cm ⁻¹) even under reflection											
A_1' modes			A_2' modes			E_1' modes			E_2' modes		
ω	P_r^a	P_b^b	ω	P_r^a	P_b^b	ω	P_r^a	P_b^b	ω	P_r^a	P_b^b
312	69.9	11.5	602	70.1	24.6	403	15.5	18.4	275	73.1	24.7
508	94.4	24.6	641	44.3	11.4	437	73.6	14.6	399	88.1	31.4 ^c
539	99.7	7.5	682	79.7	54.6 ^c	513	95.2	36.3 ^c	535	92.9	25.5
589	98.4	50.2 ^c	861	84.0	27.4 ^c	611	93.7	21.9	612	89.8	40.5 ^c
738	94.3	2.4	937	18.2	13.4	636	68.7	22.3	640	14.4	12.9
828	30.9	3.9	1133	2.1	3.9	638	96.7	27.4	682	93.6	54.4 ^c
1192	5.1	5.5	1272	0.8	21.7	675	95.7	44.5 ^c	762	93.8	1.7
1275	2.5	25.1	1396	0.5	7.2	753	77.9	4.7	777	85.8	15.5
1295	2.4	31.7	1550	0.6	15.5	820	53.8	25.0	838	25.6	9.1
1409	1.0	35.1 ^c				877	65.2	13.1	865	33.2	17.6
1490	0.4	2.4				1008	7.1	11.1	876	70.6	15.2
1586	1.0	0.0				1033	11.4	7.7	1010	15.2	14.6
						1222	3.0	33.7 ^c	1082	11.3	27.4
						1227	4.4	4.1	1184	3.7	3.3
						1284	0.6	15.3	1213	1.3	3.8
						1359	0.4	31.9 ^c	1318	1.8	5.6
						1405	0.6	9.6	1374	1.6	17.2
						1414	1.6	19.2	1396	1.1	53.4 ^c
						1453	1.2	10.5	1417	1.2	1.2
						1531	1.5	9.2	1475	1.0	17.5
						1577	0.5	5.2	1567	0.2	6.0
									1577	0.7	1.4

Modes (in cm ⁻¹) odd under reflection											
A_1'' modes			A_2'' modes			E_1'' modes			E_2'' modes		
ω	P_r^a	P_b^b	ω	P_r^a	P_b^b	ω	P_r^a	P_b^b	ω	P_r^a	P_b^b
390	0.3	0.4	417	88.3	2.4	303	71.8	6.7	404	75.4	0.1
633	97.7	0.4	575	95.8	0.3	519	90.3	0.5	459	17.2	16.8
756	54.1	0.2	671	64.3	7.3	591	84.3	0.2	508	88.5	0.7
812	42.8	0.1	751	95.2	0.0	620	39.9	2.8	618	92.6	2.2
984	2.4	27.7	1055	11.5	15.2	650	78.6	0.7	675	46.6	11.4
1069	0.8	2.7	1238	2.1	15.7	749	91.4	0.6	741	57.8	5.0
1306	1.3	16.1	1271	4.0	0.0	808	89.1	0.6	773	90.8	1.1
1369	0.0	2.1	1454	0.7	17.9	848	27.5	12.0	832	22.7	8.3
1564	0.5	50.2 ^c	1513	0.6	24.4 ^c	891	9.2	14.0	873	67.0	6.3
			1590	1.1	2.5	986	2.6	17.7	989	17.0	3.7
						1176	6.4	6.4	1060	11.2	12.5
						1225	1.5	11.5	1188	3.2	4.1
						1260	2.2	8.0	1231	3.4	7.4
						1359	0.5	6.5	1269	1.6	9.7
						1386	0.3	0.5	1365	0.9	2.9
						1422	1.5	15.8	1383	1.2	0.1
						1497	1.0	29.9 ^c	1437	1.3	14.8
						1543	1.5	34.0 ^c	1503	0.6	58.8 ^c
						1590	0.5	22.9	1576	0.8	10.7
									1596	0.3	23.5 ^c

^a P_r is a measure of the radial character, expressed as a percentage, for each of the vibrational modes. P_r is obtained by considering the ratio of the sum of the squares of the radial components of the atomic displacements to the sum of all the squares of the atomic displacement vectors.

^b P_b is the contribution of the belt atoms to the vibrational mode, expressed as a percentage. P_b is obtained by considering the sum of the squares of the displacements of the belt atoms, normalized with respect to the square of the norm of the eigenvector.

^cIdentified as a belt mode.

note that the low-frequency modes below $\sim 900 \text{ cm}^{-1}$ tend to have predominantly radial displacements, while the higher-frequency modes tend to have predominantly tangential displacements, though exceptions to this classification are found for a number of the low-frequency modes. Also shown in Table IV for each mode is the sum of the squares of the displacements of the belt atoms P_b , normalized with respect to the sum of the squares of the

displacements of all the atoms, given as a percentage. Since modes with like symmetries mix in the dynamical matrix, the eigenvectors associated with the belt modes include some displacements of the atoms in the hemispherical caps (particularly those modes with the same symmetry and about the same frequencies). In identifying the belt modes, we select modes with the proper symmetries (given in Table III) which have the largest P_b

TABLE V. All calculated modes for C_{70} and M_6C_{70} obtained by adding a perturbation to the dynamical matrix, which causes a reduction in the restoring forces on a belt atom displaced from equilibrium in the belt plane.

Frequencies of the modes, even under reflection, expressed in cm^{-1}							
A_1' modes		A_2' modes		E_1' modes		E_2' modes	
C_{70}	M_6C_{70}	C_{70}	M_6C_{70}	C_{70}	M_6C_{70}	C_{70}	M_6C_{70}
230 ^a	269 ^a	558	536	389 ^a	328 ^a	260	247
308	294	563 ^a	540	397	381	348 ^a	317 ^a
475	437	618	563 ^a	420	397	415 ^a	371 ^a
536	462	705 ^a	619 ^a	468	409	494	451
737	678	910	867	550 ^a	503 ^a	508 ^a	456 ^a
825	814	1123	1066	574	518	620	565
1160	1156	1226	1201	623	613	685	626
1253	1260	1396	1340	719	628	705	634
1290	1288 ^a	1512	1437	744	684	809	769
1335 ^a	1302			809	782	850	798
1483	1438			982	939	856	838
1585	1495			1026	1008	980	923
				1187 ^a	1168 ^a	1070	1058
				1213	1209	1182	1186
				1262	1259	1203	1193
				1316 ^a	1282 ^a	1305	1285
				1375	1325	1325 ^a	1319
				1377	1356	1350	1326 ^a
				1430	1387	1414	1340
				1503	1427	1415	1365
				1563	1473	1548	1469
						1571	1473
Frequencies of the modes, odd under reflection, expressed in cm^{-1}							
A_1'' modes		A_2'' modes		E_1'' modes		E_2'' modes	
C_{70}	M_6C_{70}	C_{70}	M_6C_{70}	C_{70}	M_6C_{70}	C_{70}	M_6C_{70}
363	350	374	349	285	271	358	340
597	543	525	444	460	419	458	428
742	670	668	664	555	510	466	438
784	744	741	678	592	551	563	515
979	934	1053	1051	632	590	656	603
1046	1003	1202	1190	716	655	703	668
1301	1280	1271	1269	796	735	768	707
1367	1338	1450	1385	839	825	803	760
1560 ^a	1452 ^a	1508 ^a	1453 ^a	874	847	859	799
		1588	1496	955	922	979	939
				1172	1167	1054	1043
				1202	1200	1179	1167
				1253	1241	1227	1225
				1345	1320	1264	1273
				1384	1349	1348	1322
				1422	1356	1371	1336
				1494 ^a	1427 ^a	1437	1366
				1540 ^a	1445 ^a	1502 ^a	1415 ^a
				1586	1485	1575	1482
						1591 ^a	1490 ^a

^aIdentified as a belt mode.

values (see Table IV), and in this way we identify modes that involve predominantly belt and cap displacements. We refer to such modes as “belt” and “cap” modes, respectively.

Among the modes given in Table IV, those that transform according to the A'_1 , E'_2 , or E''_1 irreducible representations are Raman active, with the A'_1 modes being observed in the (\parallel, \parallel) polarization geometry and the E''_1 modes observed in the (\parallel, \perp) polarization, and the E'_2 symmetry modes seen in both polarization geometries. A comparison between the calculated frequencies shown in Table IV and the measured Raman-active and infrared-active mode frequencies (see Tables VI and VII) shows an overall satisfactory agreement, especially for the high-frequency modes. The agreement is not as good for the low-frequency modes.

To obtain better agreement for the low-frequency modes, we add a perturbation to the dynamical matrix as discussed above. We assume that the force constants for C₆₀, which are used in the calculation of the eigenfrequencies in C₇₀, overestimate the shear restoring forces between the belt atoms and the two adjacent layers of atoms on both sides of the belt. The need for such a correction is expected since the C₇₀ molecule is strained in the belt region, as evidenced by the appreciable devi-

ation of the hexagonal and pentagonal angles from their ideal values.

The perturbation matrix which we introduce depends on two parameters: k_1 which is a force constant for bond bending of the bond connecting a belt atom to its first-nearest neighbor on an adjacent layer, and k_2 which is a bond-bending force constant for a bond connecting two nearest-neighbor belt atoms.

By inspecting the eigenvectors of the modes listed in Table IV, we find that the frequency of the lowest calculated belt mode with A'_1 symmetry has a value of 589 cm⁻¹ while the lowest measured Raman-active mode with A'_1 symmetry occurs at 228 cm⁻¹. We further find that the frequency of this A'_1 mode is sensitively determined by shear restoring forces for the belt carbon atoms. The reduction in these shear restoring forces, as introduced by the perturbation, is thus adjusted so as to cause a downshift in the A'_1 mode at 589 cm⁻¹ to a value of 230 cm⁻¹; this mode is then identified with the Raman-active mode whose measured frequency is 228 cm⁻¹. Furthermore, the E'_2 mode which is calculated to be 275 cm⁻¹ in the absence of the mode-softening perturbation is downshifted in frequency to a value which we choose to be 260 cm⁻¹, in agreement with Raman scattering measurements (between 256 cm⁻¹ and 261 cm⁻¹

TABLE VI. Comparison between the measured and calculated Raman-active mode frequencies in C₇₀ expressed in cm⁻¹. Calculated values (model) include the effect of perturbation theory (see text).

ω (cm ⁻¹) ^a	ω (cm ⁻¹) ^b	ω (cm ⁻¹) ^c	Model	Symmetry
228			230	A'_1
258	261 ^d	256	260	E'_2
399	400 ^e (shoulder)		348	E'_2
409	411 ^e		415	E'_2
455	459 ^e		475, 460	A'_1, E''_1
508	501 ^e	517	508	E'_2
569	573 ^e	564	536, 555	A'_1, E''_1
701	704 ^d		705	E'_2
714			716	E''_1
737	739 ^d	740	737	A'_1
766	770 ^e		796, 805	E''_1, E'_2
1062	1062 ^d	1065	1070	E'_2
1165			1160	A'_1
1182	1186 ^d	1182	1182, 1172	E'_2, E''_1
1227	1231 ^d	1224	1202, 1203	E'_2, E''_1
1257	1260 ^e		1253	A'_1
1296	1298 ^e (shoulder)		1305	E'_2
1313	1317 ^e (shoulder)		1325	E'_2
1335	1336 ^e		1335	E'_2
1367	1370 ^e	1370	1350	E'_2
1447	1448 ^d		1415	E'_2
1459			1422	E''_1
1469	1471 ^e		1483	A'_1
1493			1494	E''_1
1515	1517 ^d	1513	1540, 1548	E''_1, E'_2
1565	1569 ^d	1567	1571	E'_2

^aMeasured in Ref. 9.

^bMeasured in Ref. 8.

^cMeasured in Ref. 16.

^dObserved in both (\parallel, \parallel) and (\parallel, \perp) polarizations.

^eObserved only in (\parallel, \parallel) polarization.

as given for the three different experiments in Table IV). These requirements on the amount of shift in these two vibrational modes determine the parameters introduced into the perturbation, yielding $k_1 = -0.830$ mdyn/Å and $k_2 = -0.415$ mdyn/Å. The negative sign is indicative of the fact that the perturbation acts to reduce the restoring forces that act on a belt atom if it is given a predominantly radial displacement in the belt plane. The values of the C_{70} mode frequencies, calculated to first order in perturbation theory, are listed in Table V; the values of P_r and P_b in Table IV are essentially unchanged by this perturbation. To obtain more accurate values it would be necessary to go to second-order perturbation theory.

In Table VI, we list the values of the Raman-active modes measured experimentally^{8,16} along with suggested mode assignments as deduced from this calculation. The calculated mode frequencies listed in this table include the effect of the mode-softening perturbation of the belt modes. Similarly, the corresponding calculated infrared-active mode frequencies are compared with the experimentally observed infrared frequencies in Table VII. It is noted that the agreement between the experimental values of the frequencies and the calculated ones is, overall, very satisfactory.

TABLE VII. Comparison between the frequencies, in cm^{-1} , measured by infrared absorption with our calculated frequencies and mode assignments. Calculated values ω_{calc} include the effects of perturbation theory (see text).

ω (cm^{-1}) ^a	ω (cm^{-1}) ^b	ω_{calc} (cm^{-1})	Mode
458	458	468	E_1'
535	535	525	A_2''
565	565	550	E_1'
578	578	574	E_1'
642	642	623	E_1'
674	674	668	A_2''
796	795	809	E_1'
	1086	1053	A_2''
1134	1134	1187	E_1'
	1252	1262	E_1'
	1292	1271	A_2''
	1321	1316	E_1'
1415	1414	1377	E_1'
1431	1430	1430	E_1'
1462	1460	1450	A_2''
	1562	1563	E_1'

^aMeasurements reported in Ref. 9.

^bMeasurements reported in Ref. 8.

TABLE VIII. Normal mode vibrations of C_{60} and M_6C_{60} calculated using the force constants given in Table I.

$\nu_i(\mathcal{R})$	Even parity		$\nu_i(\mathcal{R})$	Odd parity	
	Frequency (cm^{-1})			Frequency (cm^{-1})	
	C_{60} model	M_6C_{60} model		C_{60} model	M_6C_{60} model
$\nu_1(A_g)$	492	505	$\nu_1(A_u)$	1142	1089
$\nu_2(A_g)$	1468	1429			
$\nu_1(F_{1g})$	501	497	$\nu_1(F_{1u})$	505	473
$\nu_2(F_{1g})$	981	940	$\nu_2(F_{1u})$	589	602
$\nu_3(F_{1g})$	1346	1322	$\nu_3(F_{1u})$	1208	1211
			$\nu_4(F_{1u})$	1450	1409
$\nu_1(F_{2g})$	541	508	$\nu_1(F_{2u})$	367	352
$\nu_2(F_{2g})$	847	803	$\nu_2(F_{2u})$	677	627
$\nu_3(F_{2g})$	931	903	$\nu_3(F_{2u})$	1025	1062
$\nu_4(F_{2g})$	1351	1324	$\nu_4(F_{2u})$	1212	1230
			$\nu_5(F_{2u})$	1575	1488
$\nu_1(G_g)$	498	479			
$\nu_2(G_g)$	626	589	$\nu_1(G_u)$	385	366
$\nu_3(G_g)$	805	754	$\nu_2(G_u)$	789	755
$\nu_4(G_g)$	1056	1102	$\nu_3(G_u)$	929	890
$\nu_5(G_g)$	1375	1348	$\nu_4(G_u)$	961	966
$\nu_6(G_g)$	1521	1435	$\nu_5(G_u)$	1327	1295
			$\nu_6(G_u)$	1413	1357
$\nu_1(H_g)$	269	260			
$\nu_2(H_g)$	439	415	$\nu_1(H_u)$	361	355
$\nu_3(H_g)$	708	660	$\nu_2(H_u)$	543	519
$\nu_4(H_g)$	788	791	$\nu_3(H_u)$	700	655
$\nu_5(H_g)$	1102	1110	$\nu_4(H_u)$	801	760
$\nu_6(H_g)$	1217	1224	$\nu_5(H_u)$	1129	1140
$\nu_7(H_g)$	1401	1346	$\nu_6(H_u)$	1385	1358
$\nu_8(H_g)$	1575	1485	$\nu_7(H_u)$	1552	1456

III. DISCUSSION

The model considered above for C_{60} and C_{70} can be extended to treat the vibrational modes in doped fullerenes. It is observed that the Raman-active mode frequencies in solid M_6C_{60} , where M represents an alkali-metal atom, are largely *independent* of the ionic radius or mass of M . This suggests that these modes are very nearly ideal intramolecular modes, and that we should consider the anions C_{60}^{6-} as being largely decoupled from the metal cations. It should therefore be possible in a first approximation to treat the effect of doping on the vibrational modes by considering the effect of charge transfer, from the alkali-metal atoms to the fullerene molecule, on the force constants of the model. Calculations using the QCFF/PI method³³ indicate that the C_{60}^{6-} ion retains its icosahedral symmetry, but that the short C=C bond is elongated while the long C-C bond shrinks slightly. Thus the difference in bond length has been calculated to decrease from 0.06 Å in C_{60} to 0.01 Å in C_{60}^{6-} , so that for C_{60}^{6-} there is almost no distinction between the bond lengths for the C=C and C-C bonds.³⁴ Accordingly we expect the pentagonal bond-stretching force constant s_p to increase while the hexagonal bond-stretching force constant s_h will decrease. The effect of doping on s_2 and s_3 is not expected to be large because the length of the bonds connecting an atom to its second- and third-nearest neighbors does not change appreciably. A 20% reduction in the angle-bending force constants is assumed in order to obtain a good fit to the available Raman data of M_6C_{60} .⁶ The values of the force constants used in the calculation of the vibrational frequencies in M_6C_{60} are listed in Table I as the primed quantities. We note that the bond-stretching constants s_p , s_h , and s_3 change between 10% and 20% while s_2 is almost unchanged. The bond-bending force constants all change by about 20%. The results of this calculation for M_6C_{60} are shown in Table VIII. Although it may be possible to apply this model to M_3C_{60} by considering values of the force constants which are intermediate between their values in C_{60} and their corresponding values in M_6C_{60} , the situation in this case is certainly more complicated.

The metallic nature of M_3C_{60} makes the optical spectroscopic measurements harder to perform. Furthermore the Jahn-Teller coupling may lead to a ground state which is not accurately characterized by the I_h symmetry of the icosahedral point group. In M_3C_{60} , the strong electron-phonon coupling causes an extensive broadening of the H_g -derived Raman-active phonon modes, as well as frequency shifts for these modes, while other modes may be hardly affected by this coupling. Consequently it is not possible to obtain accurately the shift in phonon frequencies in M_3C_{60} as compared with those in C_{60} by simply considering a modification of the force constants due to the charge transfer; only a first-order approximation is possible.

The set of force constants used in calculating the eigenfrequencies in M_6C_{60} is used here to predict the values of the Raman- and infrared-active modes in M_6C_{70} . Using the same perturbation matrix with the same values of k_1 and k_2 as in the calculation of the vibrational frequencies in C_{70} , all the frequencies of the vibrational modes in M_6C_{70} are calculated and listed in Table V along with the corresponding irreducible representations of the D_{5h} point group according to which these modes transform. Although most of the eigenfrequencies in C_{60} and C_{70} undergo a negative shift as a result of doping, some modes, whose frequencies are sensitively dependent on the bond-stretching force constant of the pentagonal nearest-neighbor bonds, do experience an upward shift in frequency. There are no reported measurements of the frequencies of the vibrational modes in M_6C_{70} , and thus we believe that the results in Table V may be useful for the interpretation of future spectroscopic measurements on doped C_{70} .

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¹H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, *Nature (London)* **318**, 162 (1985).

²W. Krätschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, *Nature (London)* **347**, 354 (1990).

³H. W. Kroto, *Nature (London)* **329**, 529 (1987).

⁴J. R. Heath, S. C. O'Brien, Q. Zhang, Y. Liu, R. F. Curl, H. W. Kroto, F. K. Tittel, and R. E. Smalley, *J. Am. Chem. Soc.* **107**, 7779 (1985).

⁵R. Taylor, J. P. Hare, A. K. Abdul-Sada, and H. W. Kroto, *J. Chem. Soc. Chem. Commun.* **20**, 1423 (1990).

⁶Ping Zhou, Kai-An Wang, Ying Wang, P. C. Eklund, M. S. Dresselhaus, G. Dresselhaus, and R. A. Jishi, *Phys. Rev. B* **46**, 2595 (1992).

⁷P. C. Eklund, Ping Zhou, Kai-An Wang, G. Dresselhaus, and M. S. Dresselhaus, *J. Phys. Chem. Solids* **53**, 1391 (1992).

⁸D. S. Bethune, G. Meijer, W. C. Tang, H. J. Rosen, W. G.

Golden, H. Seki, C. A. Brown, and M. S. Derries, *Chem. Phys. Lett.* **179**, 181 (1991).

⁹R. A. Jishi, M. S. Dresselhaus, G. Dresselhaus, K. A. Wang, Ping Zhou, A. M. Rao, and P. C. Eklund, *Chem. Phys. Lett.* **206**, 187 (1993).

¹⁰W. Krätschmer, K. Fostiropoulos, and D. R. Huffman, *Chem. Phys. Lett.* **170**, 167 (1990).

¹¹D. S. Bethune, G. Meijer, W. C. Tang, and H. J. Rosen, *Chem. Phys. Lett.* **174**, 219 (1990).

¹²R. L. Cappelletti, J. R. D. Copley, W. Kamitakahara, Fang Li, J. S. Lannin, and D. Ramage, *Phys. Rev. Lett.* **66**, 3261 (1991).

¹³K. Prassides, T. J. S. Dennis, J. P. Hare, J. Tomkinson, H. W. Kroto, R. Taylor, and D. R. M. Walton, *Chem. Phys. Lett.* **187**, 455 (1991).

¹⁴G. Gensterblum, J. J. Pireaux, P. A. Thiry, R. Caudono, J. P. Vigneron, Ph. Lambin, A. A. Lucas, and

- W. Krätschmer, *Phys. Rev. Lett.* **67**, 2171 (1991).
- ¹⁵M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *J. Mater. Res.* **8**, 2054 (1993).
- ¹⁶D. W. Snoke, Y. S. Raptis, and K. Syassen, *Phys. Rev. B* **45**, 14 419 (1992).
- ¹⁷R. E. Stanton and M. D. Newton, *J. Phys. Chem.* **92**, 2141 (1988).
- ¹⁸F. Negri, G. Orlandi, and F. Zerbetto, *Chem. Phys. Lett.* **144**, 31 (1988).
- ¹⁹R. L. Disch and J. M. Schulmann, *Chem. Phys. Lett.* **125**, 465 (1986).
- ²⁰M. Häser, J. Almlöf, and G. E. Scuseria, *Chem. Phys. Lett.* **181**, 497 (1991).
- ²¹G. B. Adams, J. B. Page, O. F. Sankey, K. Sinha, J. Menendez, and D. R. Huffman, *Phys. Rev. B* **44**, 4052 (1991).
- ²²B. P. Feuston, W. Andreoni, M. Parrinello, and E. Clementi, *Phys. Rev. B* **44**, 4056 (1991).
- ²³A. Warshel and M. Karplus, *J. Am. Chem. Soc.* **94**, 5612 (1972).
- ²⁴Z. C. Wu, D. A. Jelski, and T. F. George, *Chem. Phys. Lett.* **137**, 291 (1987).
- ²⁵S. J. Cyvin, E. Brendsdal, B. N. Cyvin, and J. Brunvoll, *Chem. Phys. Lett.* **143**, 377 (1988).
- ²⁶D. E. Weeks and W. G. Harter, *J. Chem. Phys.* **90**, 4744 (1989).
- ²⁷R. A. Jishi, R. M. Mirie, and M. S. Dresselhaus, *Phys. Rev. B* **45**, 13 685 (1992).
- ²⁸Z. Slanina, J. M. Rudzinski, M. Togasi, and E. Osawa, *J. Mol. Struct.* **202**, 169 (1989).
- ²⁹K. Raghavachari and C. M. Rohlfiing, *J. Phys. Chem.* **95**, 5768 (1991).
- ³⁰C. Z. Wang, C. T. Chan, and K. M. Ho, *Phys. Rev. B* **46**, 9761 (1992).
- ³¹F. Negri, G. Orlandi, and F. Zerbetto, *J. Am. Chem. Soc.* **113**, 6037 (1991).
- ³²H. Xia, Q. Jiang, and D. Tian, *Chem. Phys. Lett.* **198**, 109 (1992).
- ³³F. Negri, G. Orlandi, and F. Zerbetto, *Chem. Phys. Lett.* **196**, 303 (1992).
- ³⁴P. W. Fowler, *Philos. Mag. Lett.* **66**, 277 (1992).