***Ab initio* investigation of the vibrational and geometrical properties of solid C_{60} and K_3C_{60}**

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We have used a first-principles density-functional-based method to investigate the changes in the vibrational and geometrical properties of solid C_{60} arising from doping with potassium. *Ab initio* results for all intramolecular modes of C_{60} and K_3C_{60} at the zone center and for selected external modes of the doped compound are presented. Estimates for the equilibrium structure of the C_{60} molecule for both compounds are derived. We find a doping-induced softening of the vibrational spectrum, which is especially strong for high-energy modes, and a reduction of the bond length alternation of the C-C bonds by 30%. The calculations further indicate an instability connected with the potassium ion sitting at the octahedral site.

I. INTRODUCTION

The high molecular symmetry of fullerenes is the origin of their unusual structural and electronic properties in the solid, which have been under intensive investigations since the development of an efficient production method.¹ The discovery of superconductivity in alkali-metal-doped C_{60} crystals,² which to date possess the highest transition temperatures of organic materials, has stimulated numerous work devoted to the question of the pairing mechanism. Growing experimental and theoretical evidence point to a phonon-mediated pairing picture with an electron-phonon interaction in the intermediate to strong coupling regime.³ However, some discrepancies exist regarding a quantitative description that includes, e.g., the size of individual phonon contributions to the overall coupling strength or the importance of low-energy vibrations. A main source for these uncertainties is an incomplete knowledge of vibrational eigenmodes, prohibiting reliable predictions for individual coupling strengths.⁴

In this paper, we present an *ab initio* study of the vibrational and geometrical properties of solid C_{60} and K_3C_{60} using a local-density-based pseudopotential method. Its main emphasis lies on the changes of the vibrational excitations and of the molecular geometry evoked by the alkali-metal dopants. We diagonalize the whole $\mathbf{k} = 0$ dynamical matrix to obtain frequencies and a displacement pattern of all intramolecular zone-center modes for undoped and doped compounds. This is supplemented by an investigation of selected low-energy potassium modes. We further analyze doping-induced modulations of the molecular structure with special emphasis on the change in bond alternation. Extensive comparison with available experimental data serves as a test for the accuracy of our numerical method.

The structure of an isolated C_{60} molecule belongs to the icosahedral point group I_h . Two carbon-carbon bonds can be distinguished: The pentagon-hexagon ("single") bonds are longer than the hexagon-hexagon ("double") bonds. Because of the high molecular symmetry, the 174 internal (intramolecular) modes fall into 46 distinct vibrational levels, which can be further divided into 14 optical (10 Raman and 4 infrared active) modes and 32 silent modes. Vibrations with predominantly radial displacements of carbon atoms have excitation energies of 200–900 cm^{-1} , whereas the high-energy modes (900–1600 cm^{-1}) consist of mainly tangential motions. In the solid, the remaining 6 external modes (3 librations and 3 translations) have frequencies below 100 cm^{-1} , and in the doped compound, additional optic modes of alkali ions are typically found below 150 cm^{-1} .

The rich vibrational spectrum of both undoped and doped C_{60} was extensively studied with a variety of experimental methods. Raman,^{5–7} infrared absorption,⁶ and neutron scattering^{8,9} experiments provide detailed information about the intramolecular excitation spectrum. Doping-induced frequency shifts and line broadenings were taken as indicators for strong electron-phonon coupling. However, these methods can only partially help to identify the corresponding displacement pattern, because they do not provide an unambiguous characterization of the silent modes. This difficulty is reflected by two recent attempts at complete mode assignments, which, although both based on large numbers of experimental data, differ substantially in their predictions for the silent modes.^{10,11} Therefore, additional support by theoretical calculations is imperative.

Any quantitative analysis of the superconducting state within an Eliashberg-type approach requires an accurate knowledge of the phonon spectrum. Schlüter *et al.* have demonstrated that for fullerenes the individ-

ual coupling strength depends very sensitively on the mode eigenvectors used in the calculation.⁴ For an isolated C_{60} molecule, the task of calculating eigenmodes was addressed with a variety of techniques ranging from phenomenological¹² and semiempirical¹³ models to *ab initio* methods.^{14–17} Phenomenological models often differ widely in their predictions for silent modes, although they use similar data for their parameter fits, thus emphasizing the need for a reliable, parameter-free method. Currently, the best agreement with experiment is obtained within a local-density-functional approach with a mean deviation of $\approx 2.6\%$ for Raman and IR frequencies.¹⁷ The only *ab initio* study for K_3C_{60} was carried out by Antropov *et al.*, who calculated a few selected phonons adopting a full-potential linear muffin-tin orbital (LMTO) method.¹⁸

The present work extends the above-mentioned *ab initio* investigations to K_3C_{60} . The C_{60} calculations thereby serve a threefold purpose: They (i) provide a test for our numerical method, (ii) guide mode assignments, and (iii) are used as a reference for the K_3C_{60} results. Knowledge of the full excitation spectrum for both compounds allows an approximate determination of the doping-induced structural changes.

The paper is organized as follows. The next section introduces details of the applied method. In Sec. III, we provide a thorough discussion of our results, with subsections covering the intramolecular spectrum of C_{60} and K_3C_{60} , the external modes of K_3C_{60} , and geometrical properties. A summary is given in Sec. IV.

II. METHOD

All results presented in this work are obtained within the local-density-functional approximation using a pseudopotential approach. The electronic wave functions are represented in terms of a mixed basis set consisting of a linear combination of atomic orbitals (LCAO) and plane waves. The localized functions consist of one *s* and three *p* functions per carbon site. These functions are atomic pseudo-wave-functions that are cut off at a radius R_c where they are joined smoothly to a set of plane waves. In our case we have taken into account plane waves up to a kinetic energy of 12 Ry. Details of the method can be found in Ref. 19 and applications to systems with a large number of atoms in Ref. 20. The Hedin-Lundqvist approximation for the exchange and correlation potential has been used.²¹ Brillouin-zone integrations are carried out with two *k* points in the irreducible part of the high-symmetry fcc structure. Forces on the atoms in the unit cell were also obtained which allowed for the determination of force constants and thus the force matrix. This procedure has been applied very successfully to the calculation of surface phonons.²⁰ Details of the force calculation can be found in Ref. 22. Norm-conserving pseudopotentials of the Hamann-Schlüter-Chiang type have been used for carbon as well as for potassium. The carbon potential has been used successfully for the study of diamond, graphite, and intercalated graphite²³ while the potassium potential has been used already for surface

studies.²⁴ The potassium potential includes the partial core correction.²⁵

Both C_{60} and K_3C_{60} are known to exhibit a substantial amount of disorder regarding the orientation of the C_{60} molecule. This disorder may influence intermolecular phonon modes and may lead to small modifications of low-energy intramolecular vibrations. At present, modeling of these disordered structures is beyond the computational limits of *ab initio* calculations of phonon modes. Therefore, we have chosen the orientation of the C_{60} molecule to agree with space group $Fm\bar{3}$, where the cubic axes of the crystal coincide with twofold molecular axes, and the body diagonals with threefold axes (cf. Fig. 1). For the lattice constants experimental values are taken (14.2 Å for C_{60} and 14.24 Å for K_3C_{60}).²⁶ The basic geometry of the C_{60} molecule was obtained by assuming I_h symmetry with a fixed bond ratio of 1.46/1.40 and by relaxing the molecular radius. This procedure resulted in equilibrium radii of 3.55 Å and 3.54 Å for C_{60} and K_3C_{60} , respectively. In the undoped case, the remaining atomic forces were negligible, which demonstrates that the icosahedral symmetry of the molecule is almost preserved in the crystal. On the other hand, carbon atoms were not force free in K_3C_{60} , indicating that the fully relaxed structure possesses a different bond length ratio or deviates from spherical shape owing to the presence of nearby K ions.

Frequencies and displacement patterns of all phonon modes at the Γ point can be obtained by diagonalizing the dynamical matrix

$$D(\alpha\kappa, \beta\kappa') = \frac{1}{\sqrt{m_\kappa m_{\kappa'}}} \Phi(\alpha\kappa, \beta\kappa'), \quad (1)$$

where α and β are coordinate indices, and κ, κ' denote atoms in the unit cell with masses m_κ . The force-constant matrix (FCM) $\Phi(\alpha\kappa, \beta\kappa')$ is given by the normalized change of the component F_α of the force acting on atom κ when atom κ' is displaced in direction β . In undoped C_{60} , the task of constructing this (180×180)-dimensional matrix is greatly simplified because of the high symmetry of the space group. Within $Fm\bar{3}$, only

FIG. 1. Orientation of C_{60} molecules as used in the present calculations. C1–C3 denote positions of carbon atoms which are inequivalent under the space group $Fm\bar{3}$.

TABLE I. Γ -point frequencies (in cm^{-1}) of totally symmetric modes as obtained from frozen-phonon calculations and from diagonalizing the dynamical matrix. Experimental values are taken from Refs. 33 (C_{60}) and 7 (K_3C_{60}).

	Mode	Frozen phonon	Dynamical matrix	Experiment
C_{60}	$A_g(1)$	481	481	493
	$A_g(2)$	1460	1489	1469
K_3C_{60}	$A_g(1)$	492	481	497

three carbon atoms are not equivalent (atoms C1–C3 in Fig. 1). Applying group theoretical concepts, it is thus sufficient to successively displace each of these three atoms along three orthogonal directions. However, this procedure results in a loss of inversion symmetry, which would enormously enhance the numerical effort. Therefore, actual calculations were done by displacing two opposite C atoms simultaneously to preserve inversion symmetry. Thereby, we were able to construct the FCM for even-parity modes only. To minimize anharmonic effects, atomic displacements in both directions are considered with typical values of 0.06 Å for radial displacements and 0.03 and 0.05 Å for tangential displacements parallel and orthogonal to the short (double) bonds, respectively.

To further test the accuracy of frequencies obtained from diagonalizing the dynamical matrix, we performed additional frozen-phonon calculations for the fully symmetric $A_g(1)$ and $A_g(2)$ modes using pure radial and tangential displacement patterns, respectively. These values are compared with those obtained from the even-parity FCM and with experimental frequencies in Table I. It demonstrates the high accuracy of the frozen-phonon method for both the insulating and metallic system, and allows us to estimate the numerical error introduced by determining the frequencies from the forces to be less than 4%.

The large size of the C_{60} molecule makes it possible

to extract approximate values for odd-parity frequencies, too, from the calculation of the even-parity force fields only. If the force field originating from a single displaced atom is sufficiently short ranged, the forces produced by two opposite displaced atoms do not overlap. This can be used in the following way. We introduce a cutoff R_c and keep only forces on those atoms which lie within a distance shorter than R_c from one of the two displaced atoms. This reduced force field is then used to build the whole (180×180) FCM whose eigenvalues correspond to all even and odd modes. To check the accuracy of this approximation, we will present results for $R_c=4.9$ Å where exactly half of the molecule is taken into account (29 neighbors) and for $R_c=4.0$ Å (17 neighbors). Beside the sensibility of the odd-parity frequencies from the cutoff, the change of the even-parity frequencies by introducing the cutoff can be taken as a measure for the quality of this approximation.

III. RESULTS

A. Intermolecular modes of C_{60}

As anticipated from the smallness of the forces in the basic geometry of undoped C_{60} , the crystal environment does not significantly disturb the I_h symmetry of the molecule. Except for translations and librations, one would expect a marginal influence of the cubic symmetry on the phonon dynamics as well. This is consistent with our investigation where we obtained crystal-field-induced splittings of intramolecular modes (at the Γ point) which are smaller than the numerical error of our method. This allows us to classify the mode frequencies according to irreducible representations of the I_h group. Results are shown in Tables II and III together with available experimental data and *ab initio* cluster calculations.

Table II is dedicated to Raman (A_g, H_g) and infrared (T_{1u}) modes. The calculated frequencies agree well with

TABLE II. Calculated Raman and IR modes of C_{60} for two values of the cutoff R_c are compared to experimental data of Refs. 33 and 34, and to *ab initio* results of Wang *et al.* (Ref. 17), Faulhaber *et al.* (Ref. 16), and Jones *et al.* (Ref. 15). All frequencies are given in cm^{-1} . rms denotes root-mean-square deviations with respect to experiment (in %).

Mode	Expt.	$R_c=4.9$ Å	$R_c=4.0$ Å	Wang <i>et al.</i>	Faulhaber <i>et al.</i>	Jones <i>et al.</i>
A_g	493	481	488	483	459	582
	1469	1489	1466	1529	1493	1416
H_g	270	263	251	263	249	288
	431	422	422	432	421	437
	709	717	716	713	640	787
	773	763	754	778	750	829
	1099	1080	1080	1111	1067	1106
	1248	1198	1187	1282	1200	1193
	1426	1422	1427	1469	1425	1395
	1573	1580	1571	1598	1567	1516
T_{1u}	527	514	530	533	506	614
	576	569	570	548	550	647
	1183	1143	1146	1214	1145	1127
	1429	1457	1448	1485	1446	1403
rms		2.1	2.7	2.6	4.6	8.6

experimental values, as indicated by a root-mean-square (rms) deviation of only 2% and a maximum discrepancy of 4% [H_g values for $R_c=4.0$ Å are slightly worse, with a maximum discrepancy of 7% for $H_g(1)$]. The overall agreement is comparable or better than those of other *ab initio* studies, thus indicating the high accuracy of our method.

The silent modes are listed in Table III. For C_{60} , the force-constant matrix is effectively short ranged, as can be seen from the weak dependence of the frequencies on the cutoff. The maximum relative shift is 3.1% (4.6%) for odd- (even-) parity modes. When compared with previous cluster calculations, we find large and unsystematic differences with the work of Jones *et al.*¹⁵ over the whole frequency range. On the other hand, our results are almost identical to those of Wang *et al.*¹⁷ for low-energy modes (up to ≈ 900 cm^{-1}), which are predominantly radial vibrations. In their work, Wang *et al.* have demonstrated an almost perfect one-to-one agreement of their theoretical frequencies with peaks in neutron scattering spectra of Ref. 9 below 1000 cm^{-1} , a property which is

thus shared by our results, too. (This implies negligible phonon dispersion, because experimental spectra represent weighted Brillouin-zone averages in contrast to the zone-center calculations.) Larger differences to the results of Wang *et al.* occur only in the frequency range 1000–1400 cm^{-1} (mainly tangential vibrations), where our calculation systematically predicts a softer spectrum (up to 100 cm^{-1}). This close similarity of the frequency distribution for a bulk and a cluster geometry provides a further indication of the small influence of the lattice environment on the internal molecular vibrations for insulating C_{60} .

Silent modes are not directly accessible by optic measurements, but can be observed in neutron scattering experiments. Spectra with well-resolved peaks in the lower-energy region (below 1000 cm^{-1}) have been reported, with a reduced resolution for the high-energy modes. However, these studies provide no straightforward way of assigning vibrations to a specific representation. Recently, Dong *et al.*¹⁰ and Martin *et al.*¹¹ proposed frequency assignments based on analysis of higher-order

TABLE III. Silent modes of C_{60} in cm^{-1} . Shown are the results of the present calculation for two different cutoffs, two assignments proposed by Dong *et al.* (Ref. 10) and Martin *et al.* (Ref. 11), respectively, and two theoretical works (cf. Table II). rms values (in %) refer to deviations from the present calculation.

Mode	$R_c=4.9$ Å	$R_c=4.0$ Å	Dong <i>et al.</i>	Martin <i>et al.</i>	Wang <i>et al.</i>	Jones <i>et al.</i>
T_{1g}	563	576	502	568	566	661
	826	836	976	973	825	820
	1241	1247	1358	1481	1292	1253
T_{3g}	543	540	567	541	550	514
	788	780	865	764	771	803
	800	795	914	1214	795	1129
G_g	1277	1294	1360	1544	1360	1310
	480	476	486	485	484	454
	570	574	621	961	564	517
	772	765	806	1199	763	977
	1037	1046	1076	1330	1117	1094
	1287	1279	1356	1345	1326	1326
A_u	1501	1512	1525	1596	1528	1466
	973	982	1143	1122	947	991
T_{3u}	343	333	356	353	344	363
	725	719	680	712	717	850
	945	957	1026	797	987	1009
G_u	1131	1120	1201	1038	1227	1164
	1546	1552	1577	1313	1558	1494
	348	344	400	402	356	374
	756	742	760	739	752	749
	790	792	924	753	784	936
	937	928	970	1080	977	1115
	1259	1259	1310	1290	1339	1286
	1420	1432	1446	1526	1467	1408
H_u	388	394	343	342	393	303
	527	527	563	579	534	510
	661	666	696	666	663	634
	750	749	801	828	742	909
	1176	1177	1117	1222	1230	1203
	1291	1293	1385	1242	1360	1317
	1566	1558	1559	1600	1588	1507
rms(4.9)		1.1	8.6	21.0	3.4	12.6
rms(4.0)	1.1		8.8	21.1	3.5	12.9

IR and Raman spectra and neutron scattering data. As mentioned by the latter authors, despite the use of a large number of frequencies and an extensive set of group theoretical constraints, there is still no unique assignment possible. This is reflected in significant differences between the two proposed sets (see Table III). Our calculation clearly favors the set of Dong *et al.*, although the overall agreement (rms=9%) is not as good as with the optical data. The large rms deviation of 21% to the frequency set proposed by Martin *et al.* originates mostly in the G_g and T_{3g} modes with differences larger than 400 cm^{-1} . In general, both proposed assignments tend to a harder spectrum than predicted by our calculation.

B. Intramolecular spectrum of K_3C_{60}

In the doped compound, the closeness of neighboring K ions sufficiently distorts the icosahedral symmetry of the C_{60} molecule and makes it necessary to consider the effects of the cubic environment on the vibrational spectrum. Therefore, displacements of all three inequivalent C atoms were used to build the dynamical matrix. Cubic symmetry leads to a reduction of the number of irreducible representations at the zone center (six instead of ten) and to a splitting of the fourfold and fivefold degenerate modes according to the following scheme (for even and odd representations): $A \rightarrow A$, $T_1 \rightarrow T$, $T_3 \rightarrow T$, $G \rightarrow A + T$, $H \rightarrow E + T$.

In Tables IV and V, the calculated frequencies for intramolecular modes of K_3C_{60} are arranged in such a way to be easily compared with corresponding C_{60} modes. Although now cubic symmetry produces mixing of modes which belonged to different representations of the icosahedral group, the modifications of the vibrational spectrum turned out to be small enough to allow an unambiguous assignment of C_{60} and K_3C_{60} modes based on an eigenvector analysis (scalar products between normalized eigenvectors of two assigned modes are always larger than 0.85).

The calculated frequencies of K_3C_{60} exhibit a stronger

dependence on the cutoff than in the undoped case. The rms difference between $R_c=4.9$ Å and $R_c=4.0$ Å is 3.6% for the odd modes (2.8% with even modes included). However, frequency changes are very selective. The largest shifts occur for $H_u(1)$ ($\Delta\omega=53$ cm^{-1}) and A_u (46 cm^{-1}) whereas all other modes (even and odd) change by less than 32 cm^{-1} . The sensitivity on the cutoff indicates a significant coupling between distant carbon atoms on the same molecule due to the presence of conduction electrons. As a consequence, contrary to undoped C_{60} , any phenomenological model of the intramolecular dynamics in metallic K_3C_{60} must go beyond short-range carbon-carbon interactions only.

A comparison to available experimental data is presented in Table IV. Our calculation qualitatively reproduces the softening of the $A_g(2)$ and the two H_g modes with the highest energies, although latter shifts are larger than observed. For the chosen assignment, the rms deviation with respect to experiment is 4.6% (5.0%) for $R_c=4.9$ Å (4.0 Å). This is comparable to the rms value of 4.7% obtained by Antropov *et al.* for A_g and H_g modes, only.¹⁸ Note, however, that not all Raman- and IR-active modes could be detected in the doped compound because of screening effects. Therefore, the assignment of a H_g -type mode at 723 cm^{-1} is somewhat arbitrary. If we choose to identify this mode with $H_g(4)$, the rms deviation drops to 3.7% (4.4%). A large contribution to this discrepancy comes from the $H_g(1)$ mode which undergoes a softening and a splitting of 6 cm^{-1} ($\approx 3\%$) in the calculation, which is not observed experimentally. A possible reason is our neglect of any deformation of the molecule, which may especially affect the low-energy vibrations.

Figure 2 shows a graphical comparison of the vibrational spectrum of zone-center modes of C_{60} and K_3C_{60} . It corresponds to a phonon density of states if all branches are dispersionless. The most characteristic change induced by doping is a softening of almost all the modes. This is more clearly seen in Fig. 3(a) where the shifts are plotted as a function of the mode frequency. The average decrease in frequency when doping is 22.7 cm^{-1} where the strongest softening occurs in the high-

TABLE IV. Optic modes of K_3C_{60} for two cutoffs. For convenience, corresponding modes of C_{60} are added in parentheses. Experimental values are taken from Refs. 7 (Raman) and 35 (IR). The last column shows theoretical values obtained by Antropov *et al.* (Ref. 18). All frequencies are given in cm^{-1} .

T_h (I_h)	$R_c=4.9$ Å	$R_c=4.0$ Å	Expt.	Antropov <i>et al.</i>
A_g (A_g)	481 (481)	476 (488)	497	458
	1475 (1489)	1467 (1466)	1453	1463
E_g, T_g (H_g)	252, 258 (263)	243, 250 (251)	271	281
	407, 404 (422)	407, 404 (422)	432	454
	658, 663 (716)	667, 672 (716)	723	753
	737, 740 (763)	709, 711 (754)		785
	1019, 1023 (1079)	1036, 1039 (1080)		1091
	1137, 1136 (1198)	1144, 1144 (1187)		1290
	1349, 1348 (1422)	1368, 1366 (1427)	1408	1387
	1532, 1530 (1580)	1537, 1534 (1571)	1547	1462
T_u (T_{1u})	504 (514)	509 (530)		
	562 (569)	549 (570)	573	
	1113 (1143)	1132 (1146)		
	1437 (1457)	1435 (1448)	1393	

TABLE V. Calculated frequencies (in cm^{-1}) of the silent modes of K_3C_{60} and corresponding C_{60} modes (in parentheses) for two different cutoffs.

$T_h (I_h)$	$R_c=4.9 \text{ \AA}$	$R_c=4.0 \text{ \AA}$
$T_g (T_{1g})$	543 (563)	549 (576)
	817 (826)	810 (836)
	1224 (1241)	1251 (1247)
$T_g (T_{3g})$	541 (543)	534 (540)
	772 (788)	769 (780)
	793 (800)	777 (795)
	1255 (1277)	1224 (1294)
$A_g, T_g (G_g)$	471, 473 (480)	462, 464 (476)
	571, 571 (570)	577, 577 (574)
	723, 732 (772)	723, 731 (765)
	1049, 1049 (1037)	1051, 1052 (1046)
	1280, 1277 (1287)	1279, 1278 (1278)
	1490, 1488 (1501)	1456, 1456 (1512)
$A_u (A_u)$	936 (973)	982 (982)
$T_u (T_{3u})$	344 (343)	332 (333)
	681 (725)	679 (719)
	930 (945)	925 (957)
	1139 (1131)	1146 (1120)
	1551 (1546)	1529 (1552)
$A_u, T_u (G_u)$	360, 355 (348)	339, 342 (344)
	750, 755 (756)	736, 740 (742)
	773, 770 (790)	773, 768 (792)
	926, 924 (937)	898, 897 (928)
	1254, 1248 (1259)	1238, 1233 (1259)
	1334, 1341 (1420)	1343, 1350 (1432)
$E_u, T_u (H_u)$	375, 375 (388)	428, 428 (394)
	492, 494 (527)	489, 491 (527)
	668, 668 (661)	643, 642 (666)
	702, 694 (750)	706, 698 (749)
	1077, 1074 (1175)	1101, 1099 (1177)
	1278, 1281 (1291)	1280, 1281 (1293)
	1500, 1502 (1566)	1503, 1504 (1558)

energy part of the spectrum ($>1000 \text{ cm}^{-1}$). Notably, all H_g modes in this energy range as well as $G_u(6)$ and $H_u(8)$ shift by more than 50 cm^{-1} , and $H_u(6)$ even by 100 cm^{-1} . To demonstrate that these softenings are not an artifact of the cutoff sensitivity of K_3C_{60} , we have included a similar graph comparing two spectra of K_3C_{60} obtained with different cutoffs [Fig. 3(b)]. Here, the average mode shift is only 0.9 cm^{-1} .

Similar softening effects evoked by doping with alkali metals are observed in graphite intercalation compounds and are well known to be the result of a weakening of C-C bonds because of a charge transfer from the intercalated ion to the graphitic layers.²⁷ This physical picture applies for K_3C_{60} , too, where each K atom donates one electron, leading to a C_{60}^{3+} configuration.

C. External modes in K_3C_{60}

The intermolecular vibrations of K-doped C_{60} consist of librational and translational motions of the C_{60} molecule, and of vibrations of alkali ions at tetrahedral (K1) and octahedral (K2) sites. For the chosen geometry

FIG. 2. Spectra of intramolecular vibrations of C_{60} (lines) and K_3C_{60} (solid area). Shown are the zone-center frequencies obtained with the cutoff $R_c=4.9 \text{ \AA}$ and broadened by a Gaussian function with a standard deviation of 6 cm^{-1} .

FIG. 3. Differences of mode frequencies (a) between calculated spectra C_{60} and K_3C_{60} , and (b) between K_3C_{60} spectra obtained with $R_c=4.9 \text{ \AA}$ and $R_c=4.0 \text{ \AA}$

with space group $Fm\bar{3}$, the corresponding 15 degrees of freedom split at zone center into two T_g (librons and symmetric motion of K1) and three T_u modes (one acoustic and two optic vibrations involving C_{60} translations and antisymmetric motions of K1 and K2).

To obtain the even-parity K1 mode, we calculated the change in forces on C and K ions for a symmetric displacement of two K1 ions and diagonalized the (93×93)-dimensional dynamical matrix. We found that the coupling between a C_{60} molecule and K1 does not alter the even-parity intramolecular modes within the numerical accuracy of our method. The impact of this coupling on the low-energy libration is not negligible. However, because of the wide range of frequencies covered by the intramolecular spectrum, librational frequencies are very sensitive to small numerical errors in the force constants and therefore cannot be determined reliably using the whole dynamical matrix. On the other hand, the symmetric K1 frequency turned out to be numerically stable. The obtained value of 119 cm^{-1} agrees well with results obtained in neutron scattering²⁸ ($\approx 14 \text{ meV} \approx 113 \text{ cm}^{-1}$) and Raman scattering²⁹ (103 cm^{-1}) experiments.

In a corresponding investigation of the odd-parity external modes, we encountered an instability related to the octahedral K2 site. Essentially *no* change in the total energy was found for K2 displacements up to $0.02 \text{ \AA}$. We performed several tests to verify that this result is not a consequence of the chosen geometry of the C_{60} molecule or of numerical noise. This finding suggests that the K ion is subject to strong anharmonic motions, or may even occupy a low-symmetry equilibrium position away from the center of the octahedron. Support for this picture comes from crystallographic studies, where large thermal factors were observed especially for the octahedral site.³⁰ Similar findings were reported for Rb_3C_{60} .²⁶ This explanation is plausible in view of the small ion radius of K^+ ($1.33 \text{ \AA}$) and the large distance between K2 and the nearest-neighbor C atom of $3.69 \text{ \AA}$. On the other hand, the nearest-neighbor C-K distance for the tetrahedral site is only $3.27 \text{ \AA}$, for which we found a normal harmonic behavior for odd- and even-parity displacements. Unfortunately, the K2 instability prohibits an accurate determination of all external modes with odd parity because of a considerable mixing of K1, K2, and C_{60} translations at the zone center.

D. Equilibrium geometry of a C_{60} molecule

As mentioned in Sec. II, the basic geometry of the C_{60} molecule, used in the investigation of the phonon dynamics, was obtained by a variation of the radius only and did not allow for a complete relaxation of each C atom. However, an estimate of the true equilibrium geometry in the lattice (within the constraints enforced by the space group $Fm\bar{3}$) is possible with knowledge of the dynamical matrix and the remaining forces $\mathbf{F}(\kappa)$ in the basic geometry. The equilibrium position for an atom κ is obtained by displacing it from its position in the starting geometry by the vector $\mathbf{d}(\kappa)$, which in harmonic approximation is given by the inverse of the force-constant matrix:

$$d_\alpha(\kappa) = \sum_{\beta\kappa'} \phi^{-1}(\alpha\kappa, \beta\kappa') F_\beta(\kappa'). \quad (2)$$

Because the force field $\mathbf{F}(\kappa)$ possesses the full symmetry of $Fm\bar{3}$, the scalar product in (2) projects out those contributions to ϕ^{-1} corresponding to modes which are totally symmetric (A_g) representations of $Fm\bar{3}$. Therefore, results for the equilibrium geometry, which are shown in Table VI, are independent of the cutoff and are insensitive to numerical uncertainties connected to the external modes.

The calculated equilibrium geometry for undoped C_{60} compares very well with those obtained by various experimental techniques, and with theoretical studies based on local-density-approximation (LDA) or self-consistent Hartree-Fock methods. The changes induced by doping are small but significant. The average radius increases as a result of an extension of the short bond, whereas the long bond slightly shrinks. The bond length difference is reduced by almost 30% (from 0.059 to $0.042 \text{ \AA}$). In K_3C_{60} , a C_{60} molecule experiences a small deformation of its spherical shape. The distance of a C atom from the center of the molecule varies from 3.540 to $3.555 \text{ \AA}$ ($\approx 0.5\%$). The larger value corresponds to atoms C1 which have more space for outward relaxation for the chosen orientation (Fig. 1). Variations in the bond lengths are even smaller (less than 0.3%).

Self-consistent-field calculations using a model Hamiltonian suggest that bond alternation in undoped C_{60} is predominantly the result of a partially filled shell of the molecular π -electron system, and further predict a vanishing dimerization for a C_{60}^{6-} cluster.³¹ This is in agreement with the doping-induced reduction of the bond alternation found in present calculation.

An increase of the C-C bond lengths when doping with

TABLE VI. Equilibrium geometry of a C_{60} molecule in the solid. Average values obtained in the present work (within harmonic approximation) are compared to results from various experiments, LDA calculations for solid C_{60} , LDA cluster calculations (C_{60} and C_{60}^{3-}), and Hartree-Fock (HF) cluster calculations. All values are given in $\text{\AA}$.

	Method	Short bond	Long bond	Radius
C_{60}	present	1.390	1.449	3.537
	NMR ^a	1.40 ± 0.015	1.45 ± 0.015	
	x-ray ^b	1.399(7)	1.445(9)	3.545(1)
	Neutron ^c	1.391	1.455	
	LDA ^d	1.40	1.45	3.55
	LDA ^e	1.382	1.444	
	LDA (cluster) ^f	1.397	1.459	
	HF ^g	1.369	1.453	
	HF ^h	1.370	1.448	
K_3C_{60}	HF ⁱ	1.406	1.446	
	present	1.403	1.445	3.544
	LDA (cluster) ^f	1.404	1.449	

^aRef. 36.

^bRef. 37.

^cRef. 38.

^dRef. 39.

^eRef. 40.

^fRef. 16.

^gRef. 41.

^hRef. 42.

ⁱRef. 43.

alkali metals is a well-known fact for graphite intercalation compounds, and can be ascribed solely to charge transfer from the intercalant layers to the graphitic layers.³² However, there are substantial quantitative differences. A complete charge transfer from the dopants to C_{60} adds a charge of $1/20e$ to each carbon atom. The average increase in bond length, as obtained from our calculation, is only $0.0017 \text{ \AA}$, which is a factor of 3 smaller than the increase found for graphite intercalation compounds for the same charge transfer ($\approx 0.0055 \text{ \AA}$).³²

IV. SUMMARY

We have presented a parameter-free investigation of the lattice dynamics and the geometry of the molecular crystals C_{60} and K_3C_{60} . An extensive comparison with available data demonstrated the reliability of the applied method for predictions of eigenmodes for both the insulating and metallic cases, allowing an *ab initio* study of the effects of doping. In good agreement with experimental observations, we found a general softening of intramolecular vibrations with large shifts shown by many high-energy H_g modes and selected odd-parity phonons. It can be understood as a weakening of the C-C bonds caused by the additional charge on a C_{60} molecule, an effect well known from intercalated graphite. Eigenvectors provided by our calculation can serve as an accurate

input for future calculations of the coupling strength.

The even-parity potassium mode related to the tetrahedral site shows only a very weak harmonic coupling to the intramolecular vibrations. An analysis of odd-parity K modes was prevented by an apparent instability of the octahedral site, which is consistent with large thermal factors found in x-ray absorption measurements.

Doping-induced changes in the molecular structure are most prominent for the bond alternation, which is reduced by 30%. A superimposed slight increase in average bond length (and, consequently, in the molecular radius) shows a similar trend as in alkali-metal-doped graphite, albeit 3 times smaller.

The presented investigation of the dynamical and structural properties of metallic K_3C_{60} takes into account all charge-transfer effects but does not include renormalization corrections due to the phonon dynamics itself. Thus, deviations from experiment, which are beyond numerical errors, may be regarded as a signature of the electron-phonon coupling.

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FIG. 2. Spectra of intramolecular vibrations of C_{60} (lines) and K_3C_{60} (solid area). Shown are the zone-center frequencies obtained with the cutoff $R_c=4.9$ Å and broadened by a Gaussian function with a standard deviation of 6 cm^{-1} .