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Infrared spectra of one- and two-dimensional fullerene polymer structures: RbC$_{60}$ and rhombohedral C$_{60}$

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We compare the infrared spectra of two types of fullerene polymers: the linear-chain RbC$_{60}$ and the two-dimensional pressure-polymerized rhombohedral C$_{60}$. Both the splitting of the F_{1u} modes and the structure of newly activated lines are in agreement with fully ordered structures of molecular symmetry D_{2h} and D_{3d}, respectively. [S0163-1829(97)04318-X]

Polymeric forms of C$_{60}$ have been rapidly growing in number and diversity in the last few years.[1] Three different routes were used for their preparation: photopolymerization,[2] pressure-induced polymerization,[3] and reaction with alkali metals.[4] The first two methods yield neutral polymers, while the last one produces a 1:1 fulleride salt whose structure consists of C$_{60}^{-}$ monoanions. The detailed structure of the photopolymer is not yet known, but there exist high-precision structural refinements of the alkali fulleride polymers[5] which are arranged in linear chains, with hexagon-hexagon double bonds connecting each ball to two neighboring molecules. For the pressure-polymerized phases, analogous structures were suggested based on model calculations.[6,7] According to these models, in rhombohedral C$_{60}$ (rh-C$_{60}$) which forms at 50 kbar and 500–800 °C, the bonds are identical but each ball is connected to six neighbors instead of two. The result is a two-dimensional polymer network.

From the point of view of molecular structure, these substances represent an amazing variety of several distorted forms of the icosahedral C$_{60}$ ball. Vibrational spectroscopy is particularly suited for the investigation of symmetry re-

duction in fullerene derivatives and a large number of results has appeared,[8,9] Raman spectroscopy clearly dominating. Of particular interest is a recent comparison of the Raman spectra of RbC$_{60}$ and the low-temperature polymerized orthorombic C$_{60}$ phase[12] by Winter *et al.*, who found one-to-one correspondence between the Raman-active vibrations, indicating identical structure. Infrared measurements were reported on several pressure-polymerized phases,[3,10,11] but no systematic analysis has appeared so far.

In this paper we compare the infrared spectra of RbC$_{60}$ and rh-C$_{60}$. The main spectral features can be perfectly described by the molecular symmetry determined by the bonding pattern, in accordance with the crystal structure. We also discuss variations caused by the addition of charge.

RbC$_{60}$ and rh-C$_{60}$ were synthesized as described previously[3,5] and characterized by x-ray diffraction as single phases. Infrared spectra were taken by a Bruker IFS-28 Fourier transform interferometer in KBr pellets with 1 cm^{-1} resolution at room temperature.

Figure 1 shows the spectra in the whole vibrational range, and a C$_{60}$ spectrum for comparison. The purity of the samples is evidenced by the absence of C$_{60}$ lines. Besides
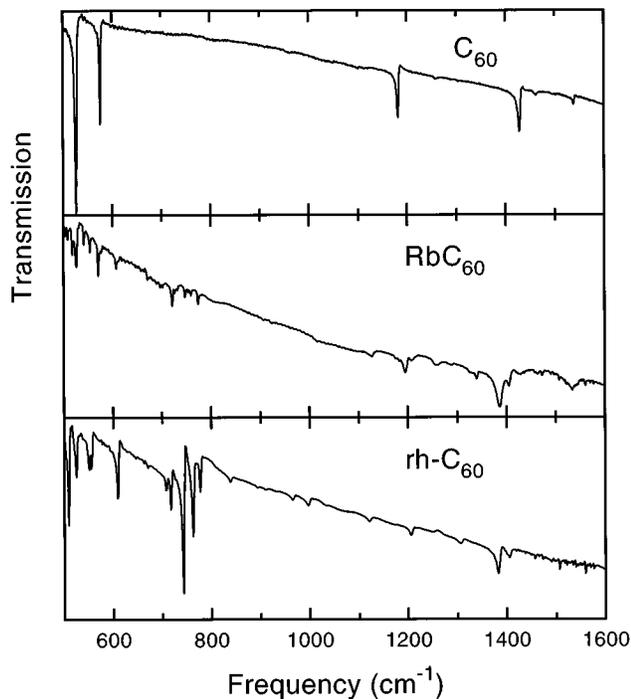
FIG. 1. Transmission of C_{60}, RbC_{60}, and rhombohedral C_{60} in the whole midinfrared range.

FIG. 2. Comparison of the infrared transmission of RbC_{60} and rhombohedral C_{60} in the region of the F_{1u} vibrations. The position of the F_{1u} modes in C_{60} is denoted by bars. The arrows indicate suggested split lines.

spectral activity in the range of the four F_{1u} modes (the only IR-active ones in I_h symmetry), a typical clustering of lines is apparent in the $700-800$ cm^{-1} range. (This is also the case for the photopolymer.[2]) Whereas these lines have relatively small intensity in the charged polymer RbC_{60}, they dominate the spectrum in rhombohedral C_{60}. Concerning the overall appearance, our spectra agree with those of other authors;[11,13] however, no detailed explanation based on symmetry was given before, which we will now attempt.

The molecular point group of C_{60} is reduced from I_h to D_{2h} in the chains[5] and to D_{3d} in the rhombohedral planes.[6,7] Table I shows the correlation for the vibrational modes of these point groups, starting from icosahedral symmetry and effectively treating the distortions as small enough perturbations so that the resulting modes still can be related to the vibrations of C_{60} itself. Under ''splitting'' we also denote the expected maximum number of infrared or Raman-active modes determined by selection rules. Because the inversion center is retained in both D_{2h} and D_{3d}, only the odd fundamentals will result in infrared activity.

Figure 2 demonstrates the feasibility of this perturbational approach, showing the splittings of the main C_{60} modes exactly as predicted by Table I. In the one-dimensional chains of RbC_{60} all four modes completely lose their degeneracy and appear as triplets [$F_{1u}(1)$: 509, 517, 526; $F_{1u}(2)$: 541, 554, 571; $F_{1u}(3)$: 1127, 1195, 1209; $F_{1u}(4)$: 1340, 1387, 1406 cm^{-1}], whereas in the two-dimensional rhombohedral C_{60} network the splitting is only twofold [$F_{1u}(1)$: 509, 525; $F_{1u}(2)$: 550, 555; $F_{1u}(3)$: 1121, 1206; $F_{1u}(4)$: 1383, 1406 cm^{-1}] into a doubly degenerate E_u and a singly degenerate A_{2u} mode.

Incidentally, the combination of correlation splitting and selection rules causes a similar situation for almost all modes, i.e., in the linear polymer the newly activated modes should show up as triplets, and in the two-dimensional one as doublets (except for triplets from the H_u modes). Several examples of this phenomenon can be observed in Fig. 3. The left panel shows an analogous triplet-doublet splitting as the principal modes in two cases (721, 726, 734 to 708, 718; 748, 754, 760 to 744, 763), and an unchanged singlet at 774 and 777 cm^{-1}, respectively. In the right panel, the emergence of modes unique for rh-C_{60} is illustrated: a singlet at 839 cm^{-1} and a doublet (966, 997 cm^{-1}). These latter modes are, of course, also allowed in the linear polymer, but have either a negligible oscillator strength or are screened by the electronic background to be discussed below.
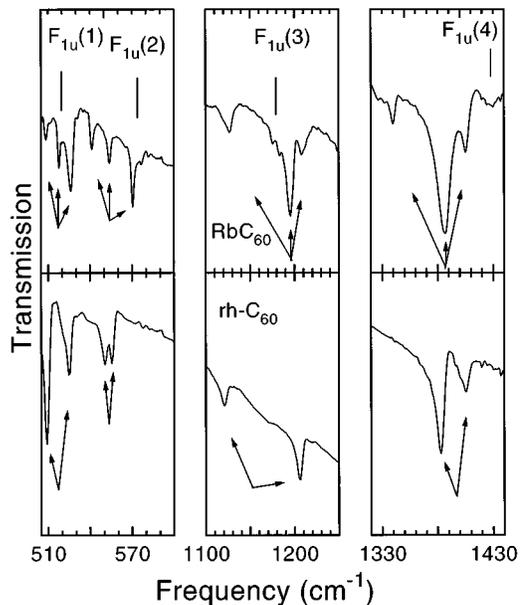
In analogy to the F_{1u} modes, the observed new multiplets point to odd C_{60} fundamental vibrations in their vicinity. This information can be useful for comparison with theoretical calculations. Unfortunately, the precision of available theoretical data is not sufficient at present for reliable assignments of our spectra. There exist, however, both semiempirical calculations[14] and fully empirical deductions[15] based on overtone and combination modes of C_{60} thick films and crystals. We show these results in the upper panels of Fig. 3. We find somewhat better agreement with the fully empirical approach by Martin et al.,[15] especially in the $700-800$ cm^{-1} range, but an unambiguous determination of the emerging lines is not possible, mainly because the number of observed lines is still far less than would be allowed by Table I. We could use the results in the table to identify peaks originating in H_u modes, if they showed up as triplets in the rhombohedral phase, but we do not see any such splitting. (The only H_u mode in both Ref. 14 and Ref. 15 which has an experimental line in its vicinity is close to the singlet at 839 cm^{-1}.) Experimental data on even less symmetric systems and more theoretical effort are needed before a full explanation of the individual lines can be given.

TABLE I. Correlation table of symmetry groups I_h, D_{2h}, and D_{3d}. Under "splitting," we denote the change in the number of expected infrared (IR) and Raman (R) active modes when the symmetry of the C_{60} ball changes from I_h to the respective point group. The total number and the symmetry species of the allowed modes are summarized in the last two rows.

I_h	D_{2h}	Splitting	D_{3d}	Splitting
$2A_g$	$2A_g$	$R\ 1\rightarrow1$	$2A_{1g}$	$R\ 1\rightarrow1$
$3F_{1g}$	$3B_{1g}+3B_{2g}+3B_{3g}$	$R\ 0\rightarrow3$	$3A_{2g}+3E_g$	$R\ 0\rightarrow2$
$4F_{2g}$	$4B_{1g}+4B_{2g}+4B_{3g}$	$R\ 0\rightarrow3$	$4A_{2g}+4E_g$	$R\ 0\rightarrow2$
$6G_g$	$6A_g+6B_{1g}+6B_{2g}+6B_{3g}$	$R\ 0\rightarrow4$	$6A_{1g}+6A_{2g}+6E_g$	$R\ 0\rightarrow2$
$8H_g$	$16A_g+8B_{1g}+8B_{2g}+8B_{3g}$	$R\ 1\rightarrow5$	$8A_{1g}+16E_g$	$R\ 1\rightarrow2$
$1A_u$	$1A_u$	$IR\ 0\rightarrow0$	$1A_{1u}$	$IR\ 0\rightarrow0$
$4F_{1u}$	$4B_{1u}+4B_{2u}+4B_{3u}$	$IR\ 1\rightarrow3$	$4A_{2u}+4E_u$	$IR\ 1\rightarrow2$
$5F_{2u}$	$5B_{1u}+5B_{2u}+5B_{3u}$	$IR\ 0\rightarrow3$	$5A_{2u}+5E_u$	$IR\ 0\rightarrow2$
$6G_u$	$6A_u+6B_{1u}+6B_{2u}+6B_{3u}$	$IR\ 0\rightarrow3$	$6A_{1u}+6A_{2u}+6E_u$	$IR\ 0\rightarrow2$
$7H_u$	$14A_u+7B_{1u}+7B_{2u}$	$IR\ 0\rightarrow3$	$7A_{2u}+14E_u$	$IR\ 0\rightarrow3$
$R\ 10\ (A_g, H_g)$	$R\ 87\ (A_g, B_{1g}, B_{2g}, B_{3g})$		$R\ 44\ (A_{2g}, E_g)$	
$IR\ 4\ (F_{1u})$	$IR\ 66\ (B_{1u}, B_{2u}, B_{3u})$		$IR\ 51\ (A_{2u}, E_u)$	

Based on the above observations, we can nevertheless conclude that the infrared spectra are in complete agreement with a well-defined crystalline material where the C_{60} units are reduced to D_{2h} and D_{3d} symmetry, respectively. There have been speculations on more random distortions leading to the loss of inversion and the consequent activation of even (Raman-active) modes in pressure-polymerized C_{60};[11] our analysis explains the whole spectrum without the need for invoking such distortions. (In fact, rh-C_{60} has higher symmetry than the linear polymer, retaining some doubly degenerate modes, and the inversion center is kept in both materials.)

The differences in the two spectra in vibrational intensity can be related to the presence of the extra electron per C_{60} unit in the charged polymer and its interaction with the molecular vibrations. In RbC$_{60}$ these electrons are correlated and the material is a one-dimensional metal.[16] The correlated electron system causes a strong background absorption in the infrared range and also screens the molecular vibrations, resulting in a smeared character of the spectrum compared to both C_{60} and rh-C_{60}. The screening can be complete for some weaker modes; this would explain why some lines which are present in rh-C_{60} are not observable in RbC$_{60}$. Another effect besides screening is coupling between the electrons and some vibrations, specifically the F_{1u} modes. This coupling occurs in C_{60}^{n-} anions, to the $t_{1u}\rightarrow t_{1g}$ electronic transition involving the extra electrons.[17] Assuming a similar mechanism involving the band formed by the molecular t_{1u} and t_{1g} orbitals, intensity enhancement (and softening, see below) should occur for the F_{1u} modes. In rhombohedral C_{60}, which consists of neutral units, the relative intensity of the infrared lines is determined solely by nuclear motion, giving a more uniform distribution of spectral weight.

There is another intriguing feature in the spectrum of rhombohedral C_{60}, the shift of the highest-frequency F_{1u} mode. This mode had been observed to have a monotonous decrease in frequency with charge n in C_{60}^{n-} anions.[18–20] From the large shift and intensity enhancement in fullerides, the coupling constant was determined to be the largest of the four for this mode.[17] Surprisingly, our spectrum of rhombohedral C_{60} shows an even larger softening from the F_{1u} position of 1429 cm^{-1} in neutral C_{60}. The interball distance in RbC$_{60}$ in the chain direction is shorter than that in the rhombohedral network, thus the hardening in the one-dimensional chains could in principle be accounted for. We cannot think of any plausible explanation, however, of the softening relative to molecular C_{60}. Network formation should harden the
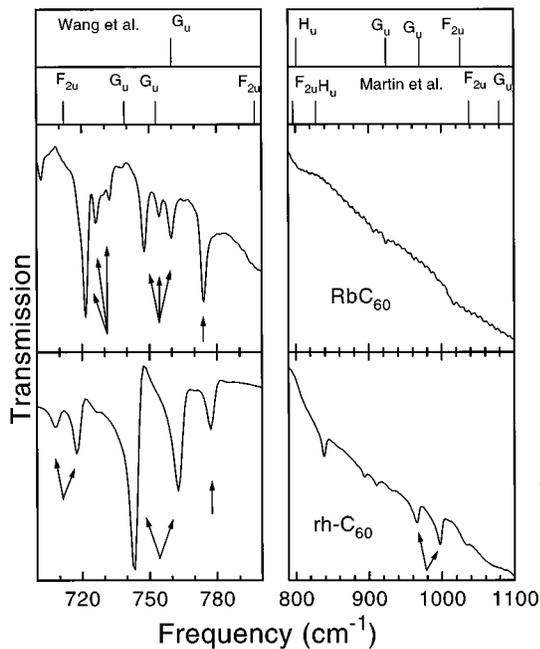
FIG. 3. New infrared modes in RbC$_{60}$ and rhombohedral C_{60} activated by symmetry reduction. The arrows indicate possible split lines. The bars in the two upper panels denote fundamental C_{60} modes according to the assignments of Refs. 14 and 15, respectively.

lattice, and there must be an additional mechanism for softening which we cannot explain at present. Raman lines in orthorombic polymers[12] (with very few exceptions) were found to soften on the addition of charge. The A_g modes also show polymerization-induced softening in the neutral state, but its magnitude (less than $10 \, \text{cm}^{-1}$) is far less dramatic than the $40 \, \text{cm}^{-1}$ shift we encounter here.

In conclusion, we compared the infrared spectra of RbC_{60} and rhombohedral C_{60} at room temperature. An analysis based on symmetry considerations revealed that the spectral features are in complete agreement with these polymers consisting of linear chains and two-dimensional planes, respectively. We also demonstrated that the symmetry reduction in these structures can be still treated as a perturbation of the original icosahedral symmetry. Therefore, new lines of the symmetry-reduced species can give reasonable estimates for frequencies of fundamental molecular vibrations in C_{60} itself.

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