



# Infrared and optical spectra of polymerized AC<sub>60</sub> fullerides

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## Abstract

We present optical spectra of polymeric AC<sub>60</sub> salts (A = K, Rb, Cs) from the far infrared through the ultraviolet. The spectra are essentially independent of the counterion and reflect the metallic character of the electronic system and the decreased symmetry of the molecular units. © 1998 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Alkali fulleride salts of composition AC<sub>60</sub> (A = K, Rb, Cs) are proven to have a polymeric structure in their stable room-temperature phase [1], forming one-dimensional chains. Detailed measurements of physical properties showed these materials to be one-dimensional metals at room temperature [1–3]. Moreover, depending on temperature and thermal history, they undergo phase transitions that change the chemical bonds between C<sub>60</sub> balls [4].

Since the existence of the  $x = 1$  compound has been suggested on the basis of high-temperature Raman measurements [5], vibrational spectroscopy has been used extensively to characterize these phases [6–12]. In this Letter, we present optical spectra of RbC<sub>60</sub>, KC<sub>60</sub>, and CsC<sub>60</sub> in a broader frequency range and with higher resolution in the infrared (IR) than previous studies. Thus we are able to identify the vibrational modes activated by symmetry reduction. A metallic absorption edge in the far-IR and

broad bands in the near-IR/visible (VIS) reflect the contribution of the electronic structure.

## 2. Experimental

RbC<sub>60</sub> and CsC<sub>60</sub> were prepared by solid-state reaction of stoichiometric quantities of the respective alkali metal and sublimed high-purity C<sub>60</sub> powder. X-ray diffraction proved them to be single-phase polymer at room temperature. The KC<sub>60</sub> crystals were produced by reacting a single crystal of C<sub>60</sub> with K, then washing the product by toluene to remove unreacted C<sub>60</sub> [13]. The C<sub>60</sub> powder used for comparison purposes was supplied by Syncom Inc. (Groningen, The Netherlands).

Spectra of the powder samples were taken on pressed pellets in paraffin (20–650 cm<sup>-1</sup>) and KCl or KBr (450–40000 cm<sup>-1</sup>), respectively, with 1 and 0.5 cm<sup>-1</sup> resolution. Low-temperature measurements were carried out in a flow-through He cryostat. We used a variety of instruments: in the near-IR and VIS, a home-made spectrometer based on a

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Perkin–Elmer monochromator and a Unicam VIS/UV spectrometer with a special attachment for highly scattering samples and, in the far- and mid-IR, several Bruker (IFS 128 and IFS 113v) Fourier-transform interferometers, including that of the National High Magnetic Field Laboratory in Tallahassee. In the latter, the magnetic field was provided by a resistive magnet producing up to 27 T. The crystalline needles of  $\text{KC}_{60}$  were measured in transmission with a Zeiss microspectrometer.

### 3. Electronic background

Pristine  $\text{C}_{60}$  and  $\text{RbC}_{60}$  could be studied in the broadest frequency range. The full spectra are given in Fig. 1. Fig. 2 shows the far-IR region in detail. A strong electronic background is obvious, with heavily screened phonon lines at the characteristic  $\text{C}_{60}$  frequencies 525 and 570  $\text{cm}^{-1}$ . We did not attempt to perform a quantitative analysis of the absorption

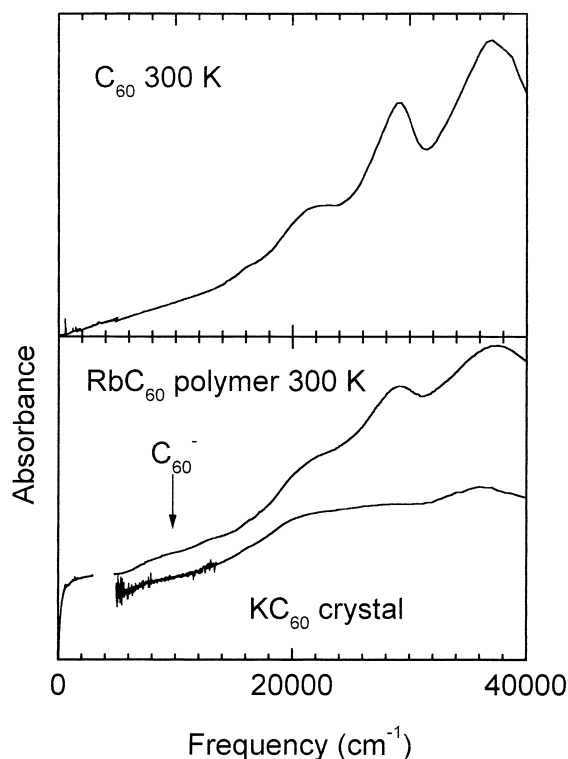


Fig. 1. Transmission of  $\text{C}_{60}$ ,  $\text{RbC}_{60}$  (powder) and  $\text{KC}_{60}$  (crystals) at room temperature in the full measured range.

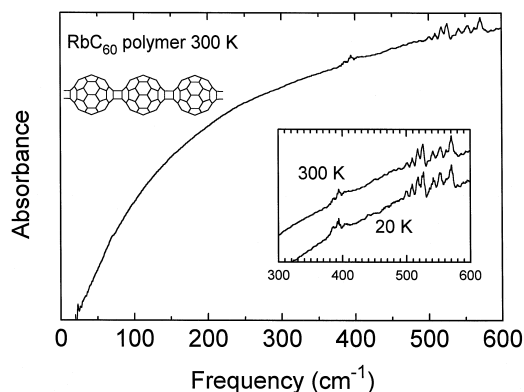


Fig. 2. Far-IR transmission of  $\text{RbC}_{60}$  at 300 K, in a paraffin pellet. Inset: Temperature dependence of the far-IR transmission of ortho-I  $\text{RbC}_{60}$  in the phonon region. The curves are shifted along the  $y$  axis for clarity.

edge, because of scattering effects in the polycrystalline pellet, but we have strong indications that the background is not of a simple Drude form. These indications come from the weak temperature dependence, shown in the inset of Fig. 2. Above 100  $\text{cm}^{-1}$ , the background is essentially constant between 20 and 300 K. The only effect of cooling is the sharpening of phonon lines. Magnetic fields of up to 25 T at 5 K caused no significant change in the spectrum. These results are in agreement with the reflectance measurements of Bommeli et al. [3] on  $\text{RbC}_{60}$  crystals, which found the optical conductivity to be independent of temperature above 100  $\text{cm}^{-1}$ . This optical conductivity is, however, still significant, a result attributed to a two-component absorption with combined plasma frequency of 5000  $\text{cm}^{-1}$ .

A strong low-frequency absorption is also apparent in the spectra of the polymers (Fig. 1, bottom part), which in fact extends much higher than 5000  $\text{cm}^{-1}$ . The monoanion  $\text{C}_{60}^-$  has a strong transition around 10000  $\text{cm}^{-1}$  [14,15], which is largely smeared out in both  $\text{RbC}_{60}$  powder and  $\text{KC}_{60}$  single crystals, a strong sign of band formation involving the  $t_{1g}$  molecular orbitals. The higher transitions at 22000, 29000 and 37000  $\text{cm}^{-1}$ , respectively (better resolved in the KCl pellets but otherwise similar), are little different from pristine  $\text{C}_{60}$ .

We also measured  $\text{KC}_{60}$  needles in polarized light but did not find any difference in the spectra taken parallel or perpendicular to the needle axis. This phenomenon occurred also in IR light [16,17] and its

explanation lies in the morphology of the needles; strictly speaking, these are not single crystals but show a complicated twinning pattern.

#### 4. Vibrational structure

The space group of the polymer is  $P2_1/m2_1/n2_1/n$  [1]. It contains two molecules per unit cell, according to two different orientations of polymer chains in the crystal. These two molecules have identical molecular symmetry, point group  $D_{2h}$ . Table 1 is the correlation table for the symmetry reduction from the isolated  $C_{60}$  molecule with  $I_h$  symmetry. We used the results of Dresselhaus et al. [18] for  $I_h \rightarrow T_h$ , along with standard literature [19,20], to produce Table 1. As shown before for pure  $C_{60}$ , crystal field effects modify the spectrum only to the second order [21–24]. Therefore we do not take correlation effects into account in the present case. Because the  $D_{2h}$  point group has only one-dimensional representations, all degeneracy is lifted and the number of IR- or Raman-active modes is reduced solely by the selection rules. The last two columns of Table 1 give the Raman- and IR-active modes. Since the molecule retains its inversion center, the mutual exclusion rule holds and, in the end, we obtain 66 IR-active and 87 Raman-active vibrations. If we

assume that the vibrational transitions of the deformed species will be reasonably close to those of undistorted  $C_{60}$ , then we can expect clusters of three lines each in the polymer spectrum, each cluster originating in a  $C_{60}$  vibration. This assumption can be justified on the grounds that significant changes in force constants will involve only four out of 60 carbon atoms and therefore this change will have a limited effect on the entire mode, which is a collective motion of the whole molecule.

The measured peak positions are summarized in Table 2; we show the measured spectra in Figs. 3 and 4. In addition to  $RbC_{60}$  and  $CsC_{60}$  at room temperature, we also measured the spectra of  $RbC_{60}$  at 20 K, to be able to better resolve individual bands.

We begin with the four well-known  $F_{1u}$  modes. We indeed see 3-fold splittings in the spectrum of  $RbC_{60}$  (Fig. 3). Splitting of the high-frequency modes has been observed before. Pichler et al. [9] have reported the highest-frequency mode to split in three components, at 1344, 1385 and 1405  $cm^{-1}$  with the combined oscillator strength unchanged; our findings are in complete accord with theirs. There is less agreement with the work of Martin et al. [12]. They report only 2-fold splittings in the two high-frequency lines, interpreting the peaks at 1385 and 1405  $cm^{-1}$  as coming from  $F_{1u}(4)$  and the ones at 1183 and 1195 from  $F_{1u}(3)$ , respectively. There is no line at

Table 1  
Correlation table of symmetry groups  $I_h$  and  $D_{2h}$

$I_h$	$D_{2h}$	Splitting
$2A_g$	$2A_g$	$R\ 1 \rightarrow 1$
$3F_{1g}$	$3B_{1g} + 3B_{2g} + 3B_{3g}$	$R\ 0 \rightarrow 3$
$4F_{2g}$	$4B_{1g} + 4B_{2g} + 4B_{3g}$	$R\ 0 \rightarrow 3$
$6G_g$	$6A_g + 6B_{1g} + 6B_{2g} + 6B_{3g}$	$R\ 0 \rightarrow 4$
$8H_g$	$16A_g + 8B_{1g} + 8B_{2g} + 8B_{3g}$	$R\ 1 \rightarrow 5$
$1A_u$	$1A_u$	$IR\ 0 \rightarrow 0$
$4F_{1u}$	$4B_{1u} + 4B_{2u} + 4B_{3u}$	$IR\ 1 \rightarrow 3$
$5F_{2u}$	$5B_{1u} + 5B_{2u} + 5B_{3u}$	$IR\ 0 \rightarrow 3$
$6G_u$	$6A_u + 6B_{1u} + 6B_{2u} + 6B_{3u}$	$IR\ 0 \rightarrow 3$
$7H_u$	$14A_u + 7B_{1u} + 7B_{2u} + 7B_{3u}$	$IR\ 0 \rightarrow 3$
IR 4	IR 66 ( $B_{1u}, B_{2u}, B_{3u}$ )	
R 10	R 87 ( $A_g, B_{1g}, B_{2g}, B_{3g}$ )	

The third column shows expected splittings of single modes, based on selection rules given in the last row. R = Raman, IR = infrared.

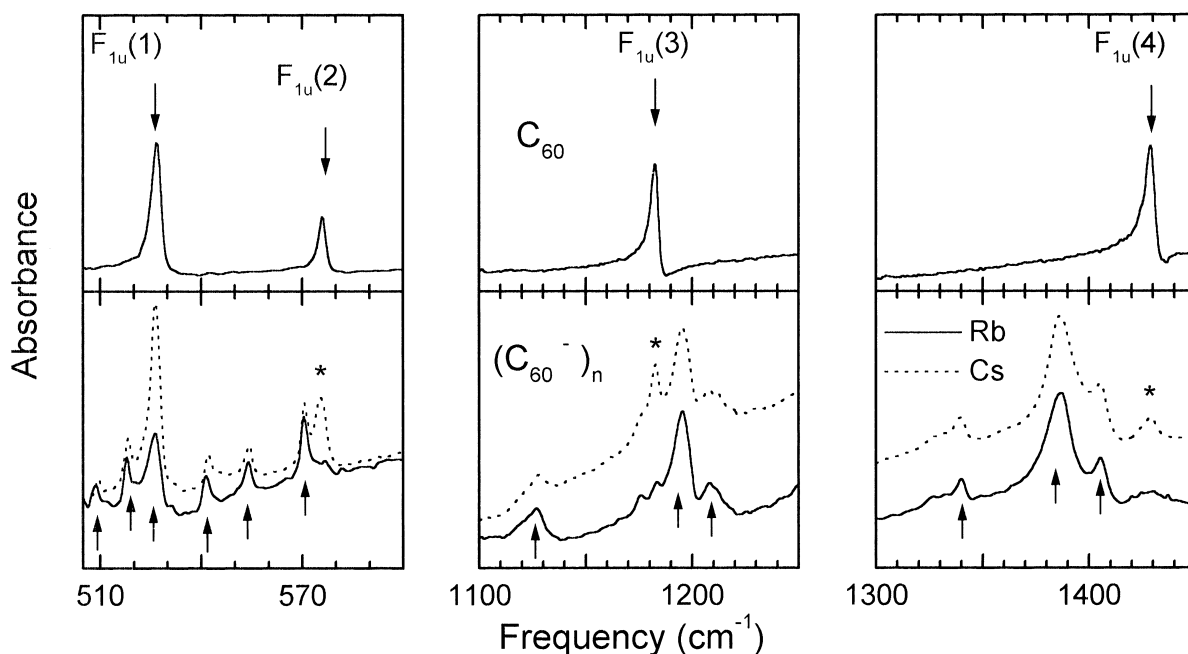


Fig. 3. Spectra of  $C_{60}$ ,  $RbC_{60}$  and  $CsC_{60}$  at 300 K in the region of the  $F_{1u}$  modes. Suggested splittings are denoted by arrows. Asterisks indicate  $C_{60}$  impurity lines in the  $CsC_{60}$  spectrum.

$1183\text{ cm}^{-1}$  in our spectra of  $RbC_{60}$ , but it appears in the  $CsC_{60}$  sample which was slightly contaminated with pristine  $C_{60}$ . Since the latter spectrum also contains two other  $C_{60}$  peaks at  $573$  and  $1429\text{ cm}^{-1}$ , and an increased intensity of the  $526\text{ cm}^{-1}$  line, we assign the  $1183\text{ cm}^{-1}$  feature not to the reduced symmetry species, but to the unperturbed  $F_{1u}(3)$  mode of neutral  $C_{60}$  impurities. Instead, we see two additional lines emerging at  $1128$  and  $1210\text{ cm}^{-1}$ . Six strong peaks evolve also between  $500$  and  $600\text{ cm}^{-1}$ , where in  $I_h$  symmetry there are only two modes at  $526$  and  $570\text{ cm}^{-1}$ . All these splittings are much higher than those found by Homes et al. [23] in the low-temperature phase of  $C_{60}$  crystals, indicating that in this case we deal with a true reduction of molecular symmetry instead of second-order solid-state effects. The splittings are, in fact, comparable to those seen by Chase and Fagan [25] in the Raman spectra of metal complexes of  $C_{60}$ . New transitions are also expected to appear; these all originate in the odd modes of the unperturbed ball. Selection rules predict lines of  $B_{1u}$ ,  $B_{2u}$  and  $B_{3u}$  to be IR active;

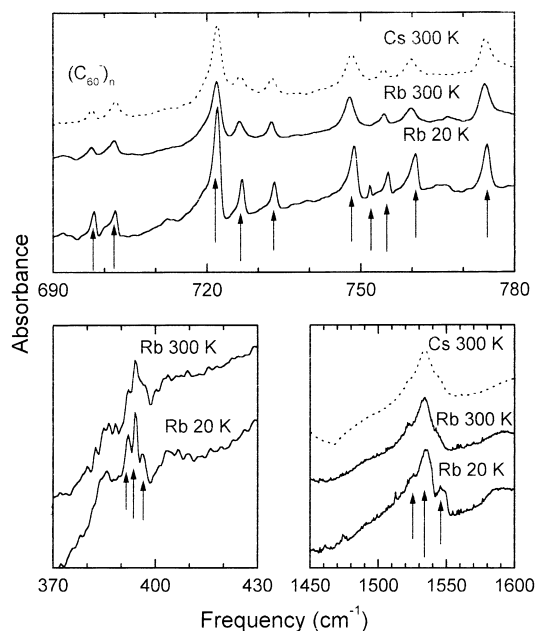


Fig. 4. Spectra of  $RbC_{60}$  and  $CsC_{60}$  in the region of activated modes of the polymer. Suggested splittings are denoted by arrows.

Table 2  
Infrared lines of  $C_{60}$  and  $RbC_{60}$  ( $CsC_{60}$  in parentheses where different from  $RbC_{60}$ ) measured at room temperature, as well as  $RbC_{60}$  at 20 K

$C_{60}$	$RbC_{60}$ ( $CsC_{60}$ )		
	300 K	20 K	
300 K	392	392	
	394	394	
	397sh	396	
	501		
	509 (510)	509	
	517 (518)	519	
	526	527 (526)	527
		541 (542)	542
		554	555
	576	570 (571)	571
607 (608)		608	
697 (698)		698	
701		702	
722		722	
726		727	
732 (733)		733	
747 (748)		749	
		752	
755		755	
760		761	
774	775		
1182	1128	1130	
	1195	1197	
	1210	1209	
	1290	1290	
	1340	1342	
	1386	1388	
	1405	1409	
1429		1522sh	
1538		1534	
		1547	

from Table 1 it follows that all these lines should exhibit a threefold splitting, i.e. if the modes are sufficiently apart, clusters of three lines are to be expected. The line at  $394\text{ cm}^{-1}$  indeed shows a clear 3-fold splitting at 20 K. We also see a significant number of new lines clustering in the region  $700\text{--}800\text{ cm}^{-1}$ . Some of them (Fig. 4) can be grouped into triplets, but not all. In any event, the low-frequency region shows very sharp well-defined lines indicating a uniform structure. The sharp vibrational pattern suggests little disorder and can be explained by assuming sufficiently long chains as has been proven by Pekker et al. for the crystalline needles [16,17].

The spectral activity between  $600$  and  $800\text{ cm}^{-1}$  is common for all  $C_{60}$  polymers known so far, notably the photopolymer by Rao et al. [26] and the polymer phases obtained at high pressure [27,28]. Recently, we showed [29] that in the latter the splitting is 2-fold, for the  $F_{1u}$  as well as the other modes, in accordance with a crystal structure where the balls have  $D_{3d}$  symmetry. The location of the activated lines suggests that many of the molecular vibrations of  $C_{60}$  fall into this region.

Although first-principles calculations on fullerene polymers exist [30,31], there is still little direct agreement with those results. The configuration closest to the  $AC_{60}$  structure is the one considered by Adams et al. [30]. They calculated the positions of the IR lines for a unit cell containing two  $C_{60}$  units of a neutral infinite chain and thus obtained twice as many lines as we expect based on our simple molecular model. The clear 3-fold splitting of the principal lines indicates that the perturbational approach based on the symmetry reduction of the balls is a reasonable starting point in the interpretation; however, this approach does not help with the assignment of the newly evolving modes. For a full understanding of the vibrational structure, we hope for an interplay between measurements on other symmetry-reduced species and further refinement of theoretical results similar to those mentioned above.

In Figs. 3 and 4, we show the spectra of both  $RbC_{60}$  and  $CsC_{60}$ . The differences in the two spectra are rather subtle and are restricted to the low-frequency end where a few lines are slightly blue-shifted in the cesium compound (Fig. 3, see the values in Table 2). The shift is below  $3\text{ cm}^{-1}$  and disappears completely in the higher-frequency lines. Despite the larger ionic radius of Cs than Rb, the interball distance was found slightly smaller in the latter compound [14]; this could explain the hardening, and the small difference accounts for the small size of the effect.

## 5. Conclusions

We have presented broadband optical and high-resolution IR spectra of the fulleride polymers  $KC_{60}$ ,  $RbC_{60}$  and  $CsC_{60}$ . We found a broad background

absorption, indicating metallic or quasi-metallic character of the electronic system, as well as clear evidence of symmetry reduction from  $I_h$  to  $D_{2h}$  in the  $C_{60}$  balls. To be able to unambiguously assign the vibrational lines, however, significantly more experimental and theoretical work is needed.

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