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Infrared and optical spectra of polymerized AC_{60} fullerides

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Abstract

We present optical spectra of polymeric AC_{60} 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_{60} ($A = K, Rb, Cs$) 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_{60} 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_{60}, KC_{60}, and CsC_{60} 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_{60} and CsC_{60} were prepared by solid-state reaction of stoichiometric quantities of the respective alkali metal and sublimed high-purity C_{60} powder. X-ray diffraction proved them to be single-phase polymer at room temperature. The KC_{60} crystals were produced by reacting a single crystal of C_{60} with K, then washing the product by toluene to remove unreacted C_{60} [13]. The C_{60} 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^{-1}) and KCl or KBr (450–40000 cm^{-1}), respectively, with 1 and 0.5 cm^{-1} 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 KC_{60} were measured in transmission with a Zeiss microspectrometer.

3. Electronic background

Pristine C_{60} and 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 C_{60} frequencies 525 and 570 cm^{-1}. We did not attempt to perform a quantitative analysis of the absorption
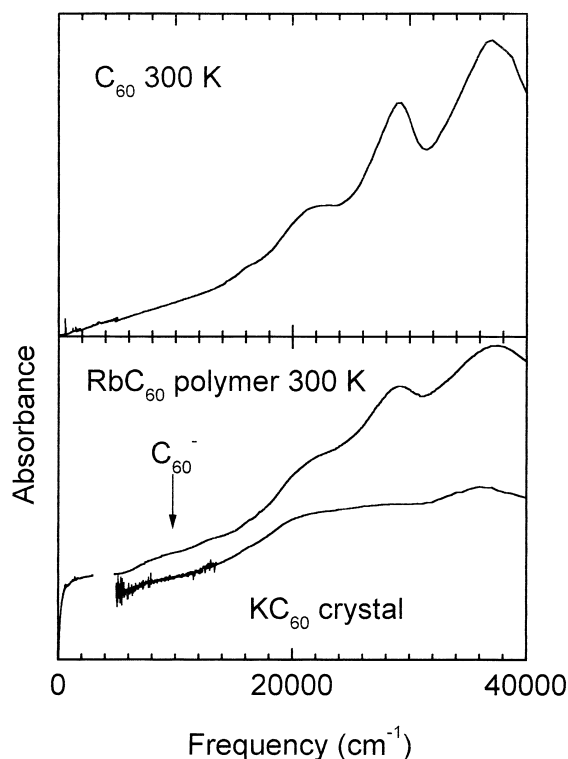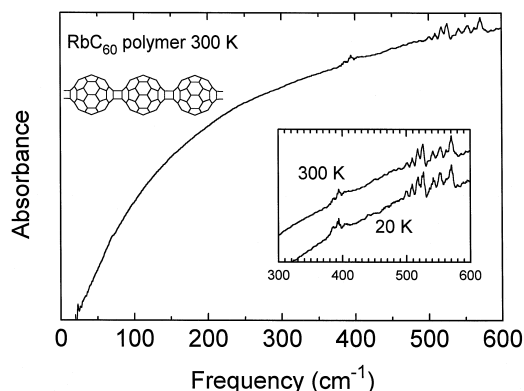

Fig. 2. Far-IR transmission of RbC_{60} at 300 K, in a paraffin pellet. Inset: Temperature dependence of the far-IR transmission of ortho-I RbC_{60} in the phonon region. The curves are shifted along the y axis for clarity.

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 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 RbC_{60} crystals, which found the optical conductivity to be independent of temperature above 100 cm^{-1}. This optical conductivity is, however, still significant, a result attributed to a two-component absorption with combined plasma frequency of 5000 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 cm^{-1}. The monoanion C_{60}^- has a strong transition around 10000 cm^{-1} [14,15], which is largely smeared out in both RbC_{60} powder and KC_{60} single crystals, a strong sign of band formation involving the t_{1g} molecular orbitals. The higher transitions at 22000, 29000 and 37000 cm^{-1}, respectively (better resolved in the KCl pellets but otherwise similar), are little different from pristine C_{60}.

We also measured 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

Fig. 1. Transmission of C_{60}, RbC_{60} (powder) and KC_{60} (crystals) at room temperature in the full measured range.

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 $P2/m2_1/n2_1/n$ [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.
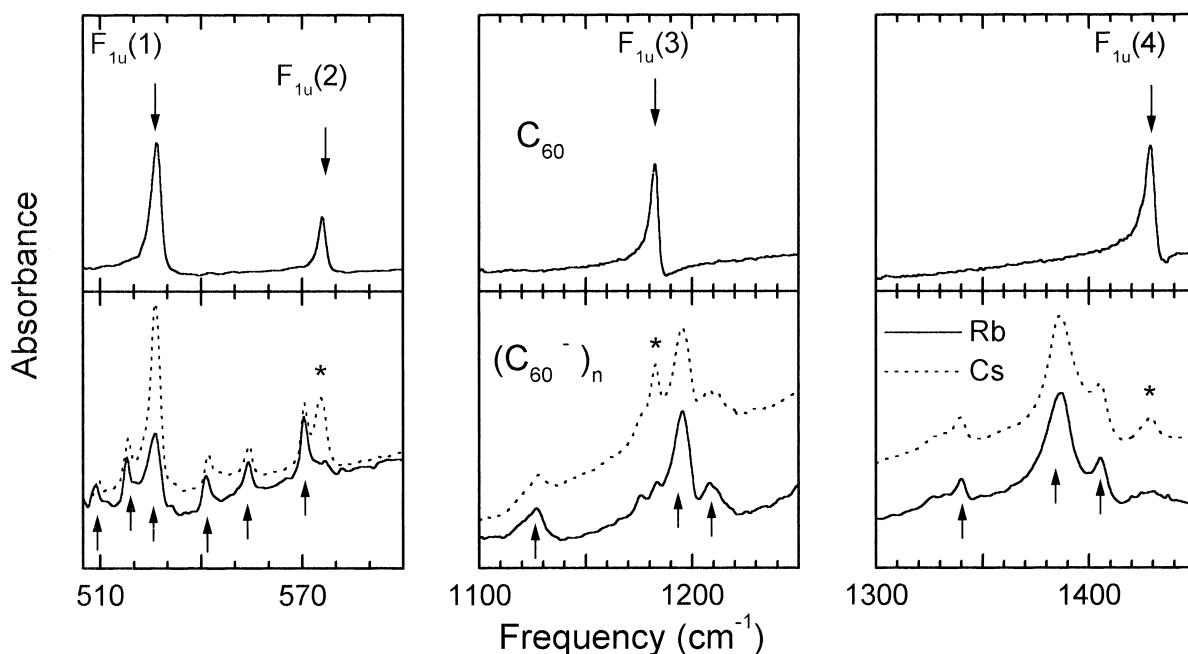R = Raman, IR = infrared.

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 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 cm^{-1}, and an increased intensity of the 526 cm^{-1} line, we assign the 1183 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 cm^{-1}. Six strong peaks evolve also between 500 and 600 cm^{-1}, where in I_h symmetry there are only two modes at 526 and 570 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;
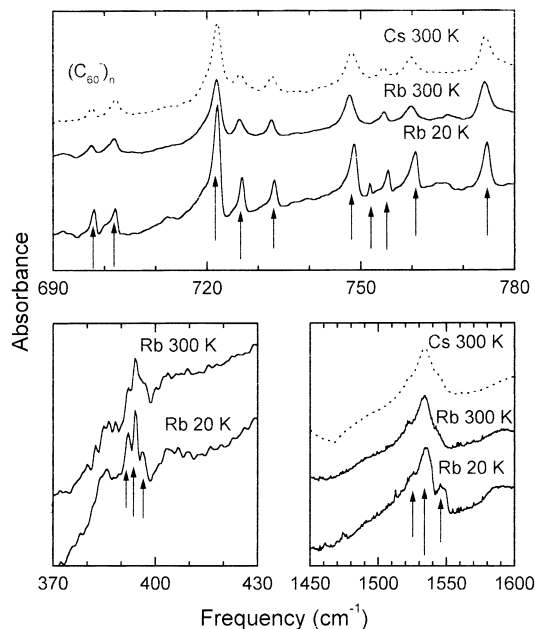

Fig. 4. Spectra of RbC_{60} and CsC_{60} in the region of activated modes of the polymer. Suggested splittings are denoted by arrows.

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	300 K	20 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 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 700–800 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 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 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.

Acknowledgements

References

[1] P.W. Stephens, G. Bortel, G. Faigel, M. Tegze, A. Jánossy, S. Pekker, G. Oszlányi, L. Forró, Nature 370 (1994) 636.

[2] S. Pekker, L. Forró, L. Mihály, A. Jánossy, Solid State Commun. 90 (1994) 349.

[3] F. Bommeli, L. Degiorgi, P. Wachter, Ö. Legeza, A. Jánossy, G. Oszlányi, O. Chauvet, L. Forró, Phys. Rev. B 51 (1995) 14794.

[4] P.W. Stephens, in: H. Kuzmany, J. Fink, M. Mehring, S. Roth (Eds.), Physics and Chemistry of Fullerenes and Derivatives, World Scientific, Singapore, 1995. p. 291.

[5] J. Winter, H. Kuzmany, Solid State Commun. 84 (1992) 935.

[6] M.C. Martin, D. Koller, X. Du, P.W. Stephens, L. Mihaly, Phys. Rev. B 49 (1994) 10818.

[7] M.C. Martin, D. Koller, A. Rosenberg, C. Kendziora, L. Mihaly, Phys. Rev. B 51 (1995) 3210.

[8] T. Pichler, R. Winkler, H. Kuzmany, Phys. Rev. B 49 (1994) 15879.

[9] T. Pichler, R. Winkler, H. Kuzmany, in: H. Kuzmany, J. Fink, M. Mehring, S. Roth (Eds.), Progress in Fullerene Research, World Scientific, Singapore, 1994 p. 261.

[10] K. Kamarás, L. Gránásy, D.B. Tanner, L. Forró, Phys. Rev. B 52 (1995) 11488.

[11] K. Kamarás, S. Pekker, D.B. Tanner, L. Forró, in: H. Kuzmany, J. Fink, M. Mehring, S. Roth (Eds.), Fullerenes and Fullerene Nanostructures, World Scientific, Singapore, 1996, p. 191.

[12] M.C. Martin, P. Wochner, L. Mihaly, L. Forró, in: H. Kuzmany, J. Fink, M. Mehring, S. Roth (Eds.), Fullerenes and Fullerene Nanostructures, World Scientific, Singapore, 1996, p. 132.

[13] S. Pekker, A. Jánossy, L. Mihály, O. Chauvet, M. Carrard, L. Forró, Science 265 (1994) 1077.

[14] M.S. Dresselhaus, G. Dresselhaus, P. Eklund, Science of Fullerenes and Carbon Nanotubes, Academic Press, San Diego, CA, 1996.

[15] V.N. Semkin, N.G. Spitsina, S. Król, A. Graja, Chem. Phys. Lett. 256 (1996) 616.

[16] S. Pekker, M. Carrard, L. Forró, L. Mihaly, in: H. Kuzmany, J. Fink, M. Mehring, S. Roth (Eds.), Fullerenes and Fullerene Nanostructures, World Scientific, Singapore, 1996, p. 110.

[17] M. Carrard, L. Forró, L. Mihaly, S. Pekker, Synth. Met. 80 (1996) 29.

[18] G. Dresselhaus, M.S. Dresselhaus, P.C. Eklund, Phys. Rev. B 45 (1992) 6923.

[19] G. Burns, Introduction to Group Theory with Applications, Academic Press, San Diego, CA, 1977.

[20] G. Burns, A.M. Glazer, Space Groups for Solid State Scientists, Academic Press, San Diego, CA, 1992.

[21] K. Kamarás, L. Akselrod, S. Roth, A. Mittelbach, W. Hönle, H.G. von Schnering, Chem. Phys. Lett. 214 (1993) 338.

[22] M.C. Martin, X. Du, J. Kwon, L. Mihaly, Phys. Rev. B 50 (1994) 173.

[23] C.C. Homes, P.J. Horoyski, M.L.W. Thewalt, B.P. Clayman, Phys. Rev. B 49 (1994) 7052.

[24] Z.H. Dong, P. Zhou, J.M. Holden, P.C. Eklund, M.S. Dresselhaus, G. Dresselhaus, Phys. Rev. B 48 (1993) 2862.

[25] B. Chase, P.J. Fagan, J. Am. Chem. Soc. 114 (1992) 2252.

[26] A.M. Rao, P. Zhou, K. Wang, G.T. Hager, J.M. Holden, Y. Wang, W. Lee, X. Bi, P.C. Eklund, D.S. Cornett, M.A. Duncan, I.J. Amster, Science 259 (1994) 955.

[27] Y. Iwasa, T. Arima, R.M. Fleming, T. Siegrist, O. Zhou, R.C. Haddon, L.J. Rothberg, K.B. Lyons, H.L. Carter Jr., A.F. Hebard, R. Tycko, G. Dabbagh, J.J. Krajewski, G.A. Thomas, T. Yagi, Science 264 (1994) 1570.

[28] A.M. Rao, P.C. Eklund, J-L. Hodeau, L. Marques, M. Nunez-Regueiro, Phys. Rev. B 55 (1997) 4766.

[29] K. Kamarás, Y. Iwasa, L. Forró, Phys. Rev. B 55 (1997) 10999.

[30] G.B. Adams, J.B. Page, O.F. Sankey, M. O'Keeffe, Phys. Rev. B 50 (1994) 17471.

[31] D. Porezag, M.R. Pederson, Th. Frauenheimer, Th. Köhler, Phys. Rev. B 52 (1995) 14963.