Interfullerene vibrations in the polymeric fulleride CsC_{60}

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The CsC_{60} fulleride at low temperatures comprises linear chains of C_{60}^- ions; the interball C–C vibrations in the chains are observed by temperature-dependent neutron spectroscopy and disappear when the transition to the high-temperature cubic phase occurs.

The structure of solid C_{60} can be understood to a good approximation using simple crystal structure arguments, based on the cubic close packing of spheroidal molecules. Such arguments can be extended to rationalize the structural properties of the intercalation compounds of fullerenes. For instance, in the superconducting alkali-metal fulleride salts with stoichiometry A_3C_{60}, the alkali-metal ions occupy the tetrahedral and octahedral interstices of a face-centred cubic (fcc) array of disordered C_{60}^{3-} ions.[1] Even though changing the size of the alkali-metal ions may affect subtly the orientational ordering of the fulleride ions, the structures remain essentially three-dimensional with interfullerene distances in excess of 3 Å.[2] However, this relatively simple picture is no longer valid when the metallic AC_{60} (A = K, Rb, Cs) salts are considered.[3] Extrapolation from the simple close packing model will predict the adoption of an fcc rocksalt structure for AC_{60}. While this is the case at temperatures above *ca.* 370 K, upon slow cooling an orthorhombic phase with pronounced one-dimensional character and unusually close contacts between the fulleride ions forms (Fig. 1).[4] Structural studies are consistent with C_{60}^- ions deformed from icosahedral symmetry and with partial covalent bonding between them along the chains, presumably as a result of [2 + 2] cycloaddition reactions.[4] This bonding picture is supported by ^{13}C solid-state NMR spectra which have provided evidence for sp^3 hybridised C atoms.[5] Here, we report the neutron spectra of CsC_{60} obtained with the neutron inelastic scattering (NIS) technique and identify the intermolecular vibrational modes, which provide the signature of interfullerence C–C bond formation in the 11–23 meV (12 meV = 8.066 cm^{-1}) energy range. These modes disappear abruptly as the transition to the high-temperature rocksalt structure occurs.

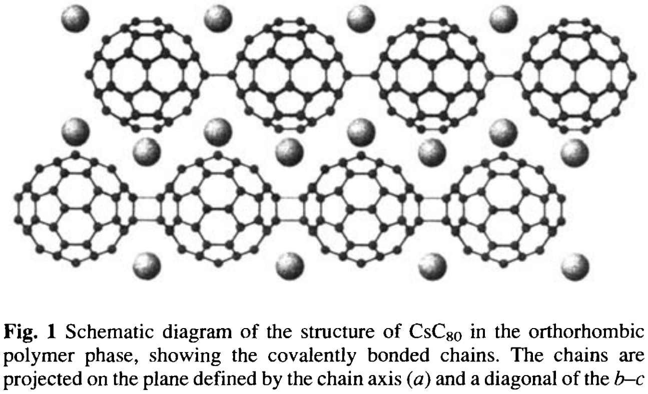

Fig. 1 Schematic diagram of the structure of CsC_{80} in the orthorhombic polymer phase, showing the covalently bonded chains. The chains are projected on the plane defined by the chain axis (*a*) and a diagonal of the *b–c* face of the unit cell; consecutive chains are related by 90° rotations about the chain axis.

The 0.4 g CsC_{60} sample was prepared by reaction of stoichiometric quantities of C_{60} and Cs in sealed quartz tubes at 800 K for four weeks with intermittent shaking. Phase purity was confirmed by high-resolution synchrotron X-ray and neutron diffraction;[6,7] the equilibrium structure is orthorhombic at 283 K with lattice dimensions a = 9.095 Å, b = 10.225 and c = 14.173 Å, and cubic at 473 K with a = 14.119 Å. Neutron inelastic scattering measurements were performed at the Institut Laue Langevin, Grenoble, using the IN6 time-of-flight spectrometer, operating in neutron-energy gain with incident neutron wavelengths of 4.12 Å at 201, 350, 419, 499 and 578 K. Additional data were also collected at 5 K with the time-focused crystal analyser (TFXA) spectrometer, operating in neutron-energy loss at the ISIS Facility, Rutherford Appleton Laboratory, UK.

Fig. 2(*a*) and (*b*) show the generalised ('neutron weighted') phonon density of states (PDOS) $G(\omega)$ of CsC_{60} between 0 and 60 meV at 499 and 201 K, respectively.† The phonon spectrum in the cubic phase at 499 K is relatively simple and is characterised by a prominent low-energy peak at 4.0 meV (with a shoulder at 6.4 meV) and major peaks at energies of 34 and 53 meV. This is reminiscent of the vibrational spectrum of pristine C_{60} in which there is a gap between the top of the band of intermolecular modes at 8 meV[8] and the lowest energy intramolecular $H_g{}^{(1)}$ mode at 33.1 meV[9] and consistent with the presence of monomeric C_{60}^- ions. The low-energy features reflect the presence of intermolecular and alkali-metal modes and their location is in agreement with earlier work on alkali-metal fulleride salts.[10,11] The spectra change little on cooling to 419 K; however, below the fcc → orthorhombic transition at 350 and 201 K, a new broad band extending from 12 to 23 meV appears. A general sharpening of the other vibrational features is also evident, especially in the vicinity of the $H_g{}^{(1)}$ mode which now appears clearly split into two components at 32.5 and 36.7 meV. The temperature evolution of the 12–23 meV band is consistent with the assignment of these modes to intermolecular C–C vibrations in the chains. We have also measured the PDOS of RbC_{60} whose low-temperature structure is identical to that of CsC_{60}; it also shows a similar broad peak in the same energy range and further supports its assignment to carbon modes with little admixture from alkali-metal ion motions. The same features as at 201 K are evident in the neutron scattering law $S(Q,\omega)$ measured at 5 K with the TFXA instrument.

Both semi-empirical and *ab initio* theoretical calculations of the vibrational properties of pristine fullerenes have been particularly successful in describing the experimental PDOS.[12] As the intermolecular interactions in these cases are dominated by van der Waals forces, the interball modes are very soft and do not extend beyond 8 meV. This is observed in the present data too at high temperatures and is consistent with the presence of monomeric C_{60}^- ions. In contrast, polymerisation introduces substantial covalent contributions to the interfullerene bonding and harder interball vibrational modes are expected. Adamset *al.*[13] have developed a first-principles quantum molecular dynamics model to describe the vibrational properties of polymerised fullerenes and their derivatives. Rigid ball–ball chain modes are predicted to occur in the energy range 10–20 meV in good agreement with the measured low-temperature neutron spectra. The predicted model excitations are all non-degenerate and their energies at the Brillouin zone centre are shown as tick marks in Fig. 2(*c*).

Above 38 meV, there is essentially a continuum of vibrational modes predicted and their detailed comparison with the experimental PDOS (to 200 meV) will be presented elsewhere. Here we note the theoretical prediction of a splitting of the lowest intramolecular peak in C_{60}, the $H_g^{(1)}$ mode, into a multiplet extending between 28.5 and 32.5 meV that is clearly evident in both the 5 and 200 K data, albeit at somewhat higher energies. The splitting disappears at high temperatures above the phase transition to the rocksalt structure and the multiplet collapses into a single peak. Optical vibrational (IR and Raman) measurements have been performed also on both bulk and thin film AC_{60} samples.[14] These studies have principally focused on the high-energy intramolecular parts of the spectra and also reveal many additional peaks compared to monomeric fullerides, arising from the reduced symmetry, including the splitting of the $H_g^{(1)}$ mode into components extending between 31.0 and 34.4 meV.

In conclusion, neutron inelastic scattering measurements of the vibrational spectra of the CsC_{60} fulleride between 5 and 578 K show evidence of C–C chain modes between 12 and 23 meV only below the fcc → orthorhombic phase transition at 370 K. Additional features in the vicinity of the lowest energy $H_g^{(1)}$ squashing mode (*ca.* 33 meV) of C_{60} are also consistent with both theoretical calculations and Raman measurements of the polymer phase. Similar results have also been obtained independently for RbC_{60}.[15]

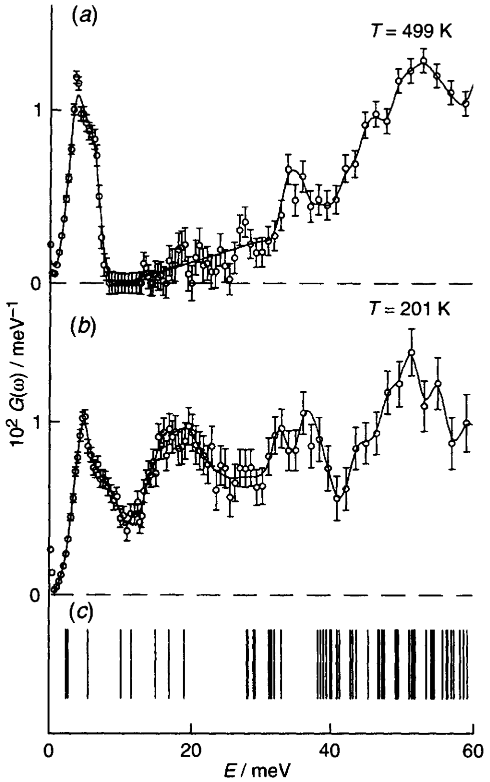

Fig. 2 (*a*), (*b*) Generalised phonon density of states $G(\omega)$ for CsC_{60} between 0 and 60 meV at 499 and 201 K, respectively. The vertical bars at each point are the estimated standard deviations. The lines are guides to the eye. (*c*) The solid bars mark the energy positions at the Brillouin zone centre of the vibrational modes in orthorhombic CsC_{60}, as calculated by a first-principles quantum molecular dynamics model[13] (1 meV = 8.066 cm^{-1}).

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Footnote

† TOF spectra were collected over the full range of scattering angles (10–115°) and summed to improve the statistics. Within the framework of the incoherent approximation, the spectral distribution function $P(\tilde{\alpha}, \beta)$ is given by $P(\tilde{\alpha}, \beta) = 2\beta\sinh(\beta/2)[S(Q,\omega)/\tilde{\alpha}]$, where $S(Q,\omega)$ is the uncorrected symmetrised scattering law and the dimensionless variables $\tilde{\alpha}$ and β are related to momentum and energy transfer through $\tilde{\alpha} = \hbar^2Q^2/2MkT$; $\beta = \hbar\omega/kT$, where M is an average atomic mass. The spectral distribution function $P(\tilde{\alpha},\beta)$ was corrected for instrumental background, Debye–Waller and multiphonon contributions using the ILL suite of programs to obtain the corrected one-phonon spectral distribution $P_1(\tilde{\alpha},\beta)$. The generalised or 'neutron-weighted' phonon DOS is then calculated through the expression $G(\omega) = \exp(2W)P_1(\tilde{\alpha},\beta)$, where $\exp(-2W)$ is the Debye–Waller attenuation factor.

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