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Vibrational Infrared Spectra of the Two Major Isomers of [84]Fullerene: C$_{84}${D_2(IV)} and C$_{84}${D_{2d}(II)}

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We present the first vibrational study of isomers of the same fullerene; C$_{84}${D_2(IV)} and C$_{84}${D_{2d}(II)}. Owing to their lower symmetry, the spectra of these isomers exhibit many more lines than the previously studied fullerenes C$_{60}$, C$_{70}$, and C$_{76}$. The temperature dependence of the IR spectra indicates a structural phase change occurs, for both isomers, near 150 K.

[84]Fullerene (C$_{84}$) is the third most abundant fullerene solvent extractable from arc-processed graphite. This is in part due to an exceptionally larger number of extractable isomers. Early ^{13}C NMR studies[1−3] indicated C$_{84}$ existed as two isomers with D_2 and D_{2d}(II) symmetry and a respective 2:1 abundance ratio. The separation of these two isomers was finally achieved only last year,[4] and the complete isolation and structural analyses of a further six, considerably less abundant, isomers of this fullerene was recently reported.[5] Vibrational studies played a crucial role in the discovery of the method of fullerene production,[6] and proved invaluable in characterizing superconducting phases in metal-doped fullerides.[7−11] However, despite this, at present only three pristine fullerenes have been studied by vibrational spectroscopy; C$_{60}$,[12−18] C$_{70}$,[10−12,19] and C$_{76}$.[20] Here, we present infrared (IR) spectra of fully purified samples of the two major isomers of C$_{84}$. Owing to their lower symmetries, the spectra of these fullerenes exhibit many more bands than that of either C$_{60}$ or C$_{70}$. We also report on the temperature dependence of these spectra, presenting the first evidence for structural phase changes in fullerene isomers.

Purification of the present samples was achieved by repeatedly recycling HPLC[4] and prepared for analysis by drop-coating gold-plated silicon substrates from toluene solution. Residual solvent was removed from the resulting films by annealing at 550 K under vacuum (P < 10^{-6} mbar) for 8 h. IR spectra were recorded between room temperature and 80 K at 10 K intervals using a Bruker IFS-66v spectrometer (0.5 cm^{-1} resolution). In each case, 64 scans were co-added to produce a final spectrum.

Figures 1 and 2 show the infrared vibrational spectra of C$_{84}$-{D_2(IV)} and C$_{84}${D_{2d}(II)}, respectively. The measured frequencies of the major bands of these isomers are listed in Table 1. In both cases, vibrational bands occur in two distinct regions: 450−850 cm^{-1} and 1050−1650 cm^{-1}. The lower frequency region contains primarily radial modes, whereas mainly tangential modes occur in the higher frequency part of the spectrum. The irreducible representation for the vibrational degrees of freedom of these D_2(IV) and D_{2d}(II) isomers are 63A + 61B_1
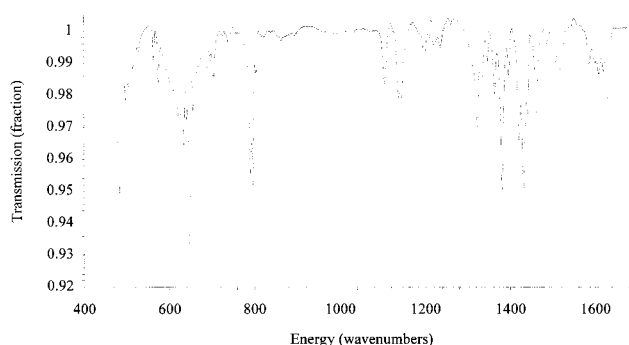

Figure 1. Vibrational infrared spectrum of purified C$_{84}${D_2(IV)}.
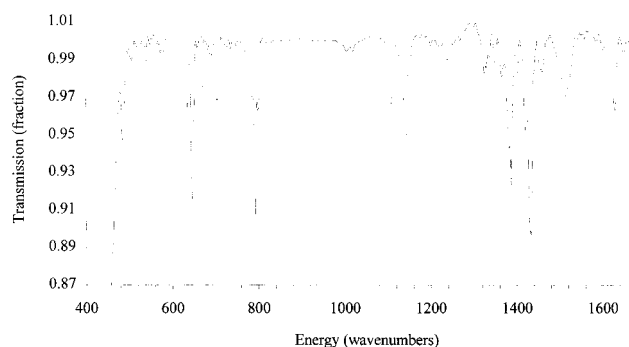

Figure 2. Vibrational infrared spectrum of purified C$_{84}${D_{2d}(II)}.

+ 61B_2 + 61B_3 and 32A_1 + 30A_2 + 31B_1 + 31B_2 + 61E, respectively. This yields 183 [61(B_1 + B_2 + B_3)] and 92 [31B_2 + 61E] discrete infrared-active vibrational frequencies for the D_2 and D_{2d} isomers, respectively. Despite the marked difference in the number of IR frequencies, both measured spectra are remarkably similar. This can be reconciled by recognizing that the these two isomers can be transformed into each other by a 90° rotation of the half of each molecule about their principal axes. Thus, there is only a small perturbation for most of the molecule on transformation, leading to many near degenerate modes.

Figures 3 and 4, respectively, show the temperature dependence of the full-width-at-half-maximum of the 1382 cm^{-1} line of C$_{84}${D_2(IV)} and the 1105 cm^{-1} line of C$_{84}${D_{2d}(II)}.[21]

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TABLE 1: Measured Infrared Vibrational Frequencies (cm^{-1}) of Distinct Bands for C$_{84}${D$_2$(IV)} and C$_{84}${D$_{2d}$(II)}^{a}

C$_{84}${D$_2$(IV)}												
484^m	498	507	516	529	565	576	621	635^m	648^s	657	688	
697	703	706	738	792^s	797^s	804	806	1009	1105^m	1139^m	1147^m	
1200^m	1223	1237	1251	1261	1324^s	1335^m	1349	1365^m	1383^s	1398	1422^m	
1432^s	1443^m	1463^m	1488	1507	1519	1524	1588	1603	1610	1621	1631^m	
C$_{84}${D$_{2d}$(II)}												
484^m	498	506	540	571	576	580	635^m	645^s	657	660	672	682
691	704^m	722	735	748	786^m	794^s	798^m	800	1004	1018	1108^m	1141^s
1238	1269	1298	1325	1330	1335	1350	1382^m	1388^s	1403	1419^m	1430^s	1433^s
1456	1461	1507	1515^m	1521	1585	1600	1609	1618	1629^m	1648	1585	

^{a} To aid the eye in reference to Figures 1 and 2, relatively strong and medium intensity bands are denoted s and m, respectively.
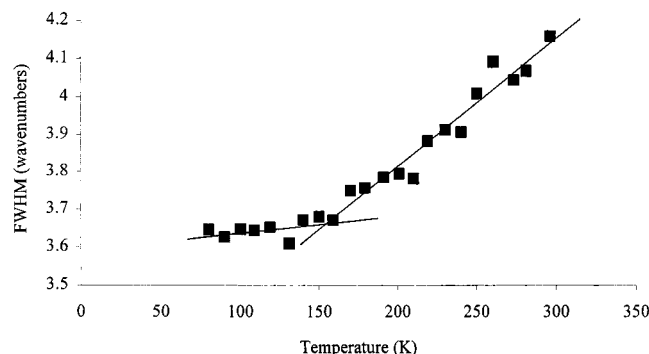

Figure 3. Temperature dependence of the fwhm for the 1382 cm^{-1} vibrational band of C$_{84}${D$_2$(IV)}. The lines were obtained by least-squares fits to the data in the 80−150 and 150−300 K temperature ranges but are intended only as a guide.
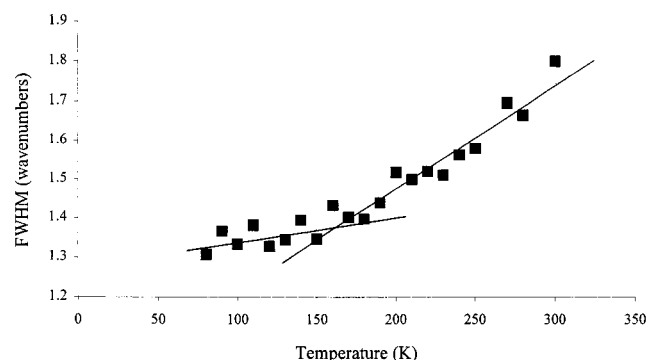

Figure 4. Temperature dependence of the HWHM for the 1105 cm^{-1} vibrational band of C$_{84}${D$_{2d}$(II)}. The lines were obtained by least-squares fits to the data in the 80−150 and 150−300 K temperature ranges but are intended only as a guide.

Infrared measurements of C$_{60}$ show an anomaly in its temperature dependence at a temperature coincident with the orientational-ordering structural phase transition.[16−18] Similar behavior (the changes in slopes in Figures 2 and 3) is observed near 150 K for both these isomers of C$_{84}$. In each case, these changes are consistent structural phase transitions observed near 150 K by preliminary analysis from a temperature-dependent X-ray diffraction (XRD) study.[22] This behavior may be contrasted with temperature-dependent XRD measurements that indicate the normal 2:1 D_2:D_{2d} mixture does not undergo a structural phase transition and retains orientational disorder even at 20 K.[23]

The literature contains several semiempirical, quantum-chemical, and ab intio theoretical vibrational studies of these particular C$_{84}$ isomers.[24−26] The calculations predict the overall appearance of the spectra with modest success. In terms of actual frequencies and intensities, however, the agreement is very poor. For example, the D_2 isomer is predicted to have only weak vibrational bands between 400 and 800 cm^{-1},[25] whereas in reality, three of the five most intense bands occur in this region.

At present, it is impossible to identify these fullerene isomers from theoretical IR spectra.

In summary, we present a vibrational infrared study of the two major isomers of C$_{84}$ [C$_{84}${D$_2$(IV)} and C$_{84}${D$_{2d}$(II)}], the first such study on isomers of the same fullerene. These studies also provided the first evidence for structural phase transitions in fullerene isomers. The present spectra add significantly to the known vibrational information on fullerenes and should benefit theoretical investigations by helping to provide more accurate force fields for fullerene skeletons.

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