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Anomalous splitting of the $F_{1u}(\rightarrow 3F_u)$ vibrations in single-crystal C_{60} below the orientational-ordering transition

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The reflectance of undoped single-crystal C_{60} has been measured from 100 to 1600 cm^{-1} at high resolution above and below the orientational-ordering transition. All of the F_{1u} modes allowed in the free molecule are observed in the solid at $\approx$ 526, 576, 1183, and 1430 cm^{-1}. Below the orientational-ordering transition, all the lines split into *quartets*, with the exception of the 576 cm^{-1} line, which narrows and remains unsplit. The appearance of quartets is attributed to the possibility of triplet splitting of the $F_{1u}(\rightarrow 3F_u)$ modes due to the local crystal field in the low-temperature phase, as well as the perturbation of the local crystal field due to the merohedral disorder, that may lead to further line splitting.

The discovery of an allotrope of carbon in the form of the C_{60} molecule[1] and the recent discovery of an efficient form of synthesis[2] have generated a great deal of interest in the physical properties of molecular crystals composed of this unusual form of carbon (which takes the form of a truncated icosahedron).

Optical probes, such as infrared (IR) and Raman spectroscopy are useful tools in determining the vibrational modes of the free molecule and in the molecular solid. In this paper, we present the first results of the temperature-dependent, high-resolution IR reflectance of single-crystal C_{60}. The normal modes of the C_{60} molecule have been previously examined.[3] Due to its exceptionally high point symmetry (I_h), the free C_{60} molecule shows just 46 distinct vibrational modes. Only the four F_{1u} modes, and the two A_g plus the eight H_g modes are IR and Raman active, respectively. To make the transition from considering the molecule to the molecular crystal, it is important to understand the structure of the solid, and the IR-active vibrations that may arise from group-theoretical considerations.

At room temperature the C_{60} molecules, unlike most molecular crystals, pack into a fcc lattice in an $Fm\bar{3}$ (T_h^3) space group, with four equivalent molecules, at T_h symmetry sites, in the unit cell.[4] At room temperature, the molecules are orientationally disordered.[5] However, at $\approx$ 260 K, the C_{60} molecules undergo orientational ordering at any of four distinct $\langle 111 \rangle$ axes.[6] Below this temperature, the molecules continue to undergo rapid reorientation until $\approx$ 90 K, at which point the rotations cease and an "orientationally ordered" phase is formed, which possesses a simple cubic (sc) unit cell in a $Pa\bar{3}$ (T_h^6) space group;[7] while the C_{60} molecules are formally at T_h sites, they are considered to possess S_6 site symmetry. In a perfectly ordered ground state, the electron-rich bond between the two hexagons (6:6) points to an electron-deficient pentagonal ring on a neighboring molecule.[7] Furthermore, the weak electrostatic repulsion of facing pentagons and 6:6 bonds along the $\langle 110 \rangle$ direction should lead to an increase in the electron density along the $\langle 100 \rangle$ direction, resulting in S_6 symmetry. A finite amount of static disorder is "frozen in" at $\approx$ 90 K and persists to very low temperature. This disorder, initially thought to be random,[8] is usually discussed in terms of "merohedral disorder"[9] (which refers to the random site-by-site population of two different standard orientations[10]). Despite the high density of "wrong" orientations (15–40%), there is still long-range orientational order in the low-temperature phase, and the average structure is still $Pa\bar{3}$. The factor-group analysis for both the high-temperature (HT) and perfectly ordered (but unobtainable) low-temperature (LT) phases has been previously determined,[11] and is shown in Table I. In the HT phase none of the IR allowed F_{1u} molecular modes are observed to split. However, in the LT phase, $F_{1u} \rightarrow A_u + E_u + 3F_u$, of which only the F_u modes are IR active. Due to the fact that the molecules possess inversion centers in both the HT and LT phases, there is no mixing of the IR and Raman modes. The presence of disorder in the low-temperature phase has further important implications for vibrational splitting.

The samples were prepared from C_{60} powder (Texas Fullerenes) which had a C_{60} purity of 99.9%. Single crystals of volumes from 0.1 to >1 mm^3 were grown by sublimation in a temperature gradient under vacuum in quartz tubes,[12] after outgassing the powder at 250 °C. The resulting crystals had a smooth, flat front surface and a curved back surface. The samples were mounted on optically black cones, and the absolute reflectance was then measured using an *in situ* overcoating technique[13]

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TABLE I. Correlation table for the high-temperature (T_h^3) and low-temperature (T_h^6) phases of solid C$_{60}$. Only the F_{1u} modes in the free molecule and the F_u modes in the solid are infrared active.

Molecule	HT phase (fcc)[a]	LT phase (sc)[b]	
I_h	T_h, T_h^3	S_6	T_h^6
$2A_g$	$2A_g$	$2A_g$	$2A_g + 2F_g$
$3F_{1g}$	$3F_g$	$3A_g + 3E_g$	$3A_g + 3E_g + 9F_g$
$4F_{2g}$	$4F_g$	$3A_g + 3E_g$	$4A_g + 4E_g + 12F_g$
$6G_g$	$6A_g + 6F_g$	$12A_g + 6E_g$	$12A_g + 6E_g + 24F_g$
$8H_g$	$8E_g + 8F_g$	$8A_g + 16E_g$	$8A_g + 16E_g + 40F_g$
A_u	A_u	A_u	$A_u + F_u$
$4F_{1u}$	$4F_u$	$4A_u + 4E_u$	$4A_u + 4E_u + 12F_u$
$5F_{2u}$	$5F_u$	$5A_u + 5E_u$	$5A_u + 5E_u + 15F_u$
$6G_u$	$6A_u + 6F_u$	$12A_u + 6E_u$	$12A_u + 6E_u + 24F_u$
$7H_u$	$7E_u + 7F_u$	$7A_u + 14E_u$	$7A_u + 14E_u + 35F_u$

[a] There are two external modes $F_g + F_u$, associated with the rotations (g modes) and translations (u modes) of the center of mass of the four C$_{60}$ molecules within the unit cell; the F_u mode is the acoustic mode.

[b] There are ten external modes $A_g + E_g + 3F_g + A_u + E_u + 3F_u$ associated with the rotations (g modes) and translations (u modes) of the center of mass of the four C$_{60}$ molecules within the unit cell; the F_u mode is the acoustic mode.

on a Bruker IFS 113V Fourier transform interferometer from 100 to 1600 cm^{-1} at resolutions of 0.4 and 0.2 cm^{-1} above and below 1000 cm^{-1}, respectively. The curved back surface of the crystal limits the interference effects to $\lesssim$ 350 cm^{-1}, which when combined with the nonreflecting nature of the cones, allows an estimated accuracy of ±1% in the reflectance.

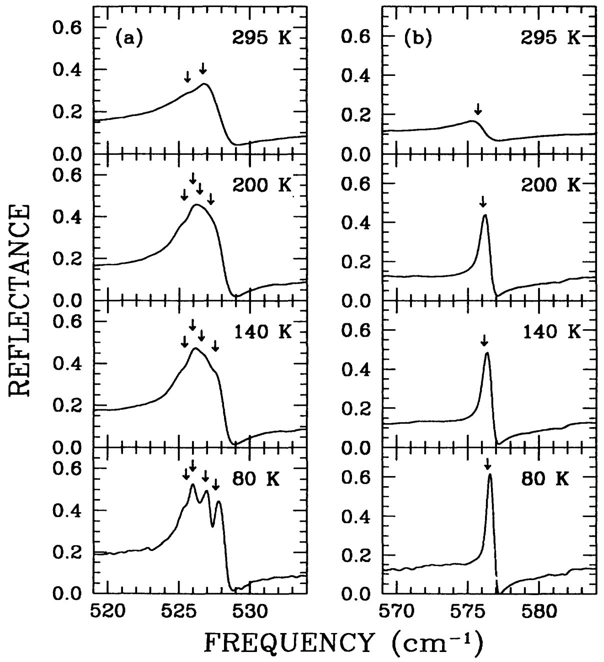

FIG. 1. The reflectance of (a) the 526 cm^{-1} feature and (b) the 576 cm^{-1} feature at 0.2 cm^{-1} in solid C$_{60}$ at 295, 200, 140, and 80 K. The arrows indicate the positions of the fitted frequencies (see Table II). Note the failure of the 576 cm^{-1} feature to show any sign of splitting or asymmetry, while the 525 cm^{-1} feature shows quartet splitting.

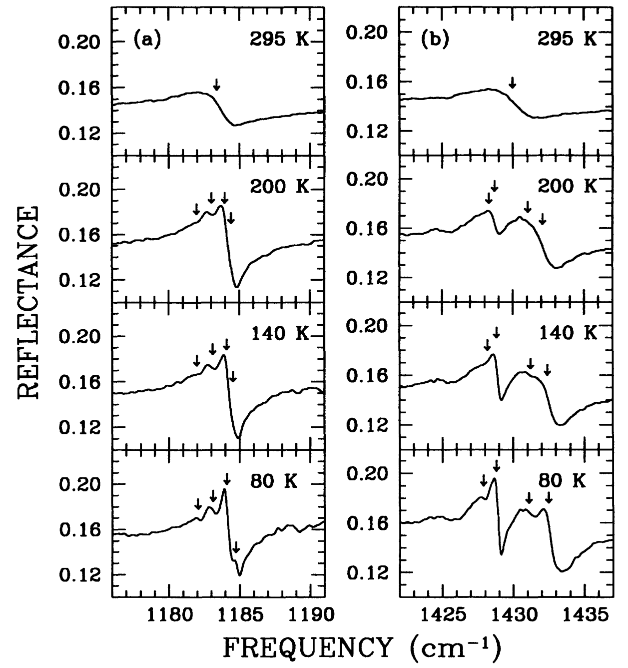

FIG. 2. The reflectance of (a) the 1183 cm^{-1} feature and (b) the 1430 cm^{-1} feature at 0.4 cm^{-1} resolution in solid C$_{60}$ at 295, 200, 140, and 80 K. The arrows indicate the positions of the fitted frequencies (see Table II). In both cases the single fundamental at room temperature splits into a quartet in the orientationally ordered phase.

The results for the reflectance at 295, 200, 140, and 80 K are shown in the regions of the four strongest features at ≈ 525 and 576 cm^{-1} in Figs. 1(a) and 1(b) with a resolution of 0.2 cm^{-1}, and at ≈ 1183 and 1430 cm^{-1} in Figs. 2(a) and 2(b) with a resolution of 0.4 cm^{-1}. The features show dispersionlike line shapes superimposed on a background reflectance of about 15%, consistent with other measurements of the reflectance below the band edge (≈ 1.8 eV) on thin films.[14] The line shapes in the reflectance have been fitted using a nonlinear least-squares technique to one or more Lorentzian oscillators in the form of a complex dielectric function $\tilde{\epsilon} = \epsilon_r + \imath\epsilon_i$:

$$\tilde{\epsilon}(\omega) = \epsilon_\infty + \sum_j \frac{\omega_{pj}^2}{\omega_j^2 - \omega^2 - \imath\omega\gamma_j} \qquad (1)$$

where ϵ_∞ is a constant term in the dielectric function, and ω_j, γ_j, and ω_{pj} are the frequency, width, and oscillator strength of the jth vibration. The reflectance is calculated from the real (n) and imaginary (k) indices of refraction, $R = [(n-1)^2 + k^2]/[(n+1)^2 + k^2]$, where $n = [\frac{1}{2}(\sqrt{\epsilon_r^2 + \epsilon_i^2} + \epsilon_r)]^{1/2}$, and $k = [\frac{1}{2}(\sqrt{\epsilon_r^2 + \epsilon_i^2} - \epsilon_r)]^{1/2}$. The results of the fits to the data at 295 and 80 K are summarized in Table II. The errors for the fitted values (which have been calculated in the usual way from the covariance[15]) are quite small, indicating that data is described quite well by simple oscillators.

At 295 K, the line at ≈ 525 cm^{-1} is seen to be a doublet, with a strong vibration at 526.6 cm^{-1}, and a weaker

TABLE II. The fitted parameters for the vibrational features at ≈ 526, 575, 1183, and 1430 cm^{-1} at room temperature and at 80 K; the errors are indicated in parenthesis. All units are in cm^{-1}. The values of ϵ_∞ returned from the fits varied from ≈4–5, in rough agreement with the values for ϵ_1 below the band gap as measured by ellipsometry on C$_{60}$ films (after Kelly *et al.*, Ref. 14).

295 K				80 K		
ω_i	γ_i	ω_{pi}		ω_i	γ_i	ω_{pi}
			{	525.42 (0.02)	0.33 (0.03)	33.6 (2.3)
525.51 (0.03)	1.50 (0.08)	45.2 (2.3)		525.88 (0.01)	0.57 (0.02)	75.7 (1.5)
526.56 (0.01)	1.78 (0.02)	81.1 (1.2)		526.64 (0.01)	0.72 (0.02)	51.3 (1.3)
				527.54 (0.01)	0.44 (0.01)	25.3 (0.4)
575.73 (0.01)	1.69 (0.01)	49.7 (0.2)	→	576.40 (0.01)	0.20 (0.01)	48.7 (0.3)
1183.42 (0.01)	2.48 (0.03)	49.6 (0.2)	{	1182.04 (0.11)	0.40 (0.17)	6.5 (1.9)
				1183.12 (0.04)	0.52 (0.08)	17.4 (1.3)
				1184.11 (0.01)	0.56 (0.03)	37.9 (1.0)
				1184.74 (0.04)	0.40 (0.06)	14.3 (1.6)
1430.00 (0.01)	3.19 (0.03)	55.1 (0.2)	{	1427.92 (0.05)	0.42 (0.08)	13.1 (1.2)
				1428.83 (0.01)	0.45 (0.01)	36.6 (0.5)
				1431.11 (0.03)	1.16 (0.07)	33.1 (1.1)
				1432.48 (0.01)	1.13 (0.03)	51.2 (0.7)

line at 525.5 cm^{-1}; the other lines are best fit using a single Lorentzian with frequencies of 575.7, 1183.4, and 1430.0 cm^{-1}; these frequencies are very close to those seen in C$_{60}$ thin films,[2,16] where four strong absorptions are seen at 528, 577, 1183, and 1429 cm^{-1} (in turn, these frequencies are similar to the four observed F_{1u} modes in the free C$_{60}$ molecules[17]). The origin of the doublet at ≈ 525 cm^{-1} may be due to the crystal lattice imposing some degree of preferential orientation on the molecules, even though dynamical measurements such as NMR indicate a high degree of rotational disorder.[5] Whether or not this would be sufficient to lift the degeneracy of the F_{1u} mode[18] and create the doublet at ≈ 525 cm^{-1} is unclear. While *ab initio* calculations of the fundamental frequencies of vibration allow for the possibility of an accidentally degenerate non-F_{1u} mode,[19,20] recent experimental assignments of the normally silent modes[21] indicate that there are no fundamental vibrations of either even (g) or odd (u) parity that lie close to the F_{1u} modes, ruling out any accidental degeneracies.

As the crystal is cooled through the orientational-ordering transition down to 80 K, all the modes are observed to split into *quartets*, with the exception of the line at ≈ 576 cm^{-1} which remains *unsplit*, and hardens slightly while narrowing to the instrumental resolution. This result is a significant refinement of earlier absorption work done on C$_{60}$ thin films,[22] which showed the 1430 cm^{-1} line splitting into only two components, and an asymmetry in the 1183 cm^{-1} feature developing below the orientational-ordering transition (the two low-frequency modes were not observed). The ability of reflectance spectroscopy to observe fine structure, whereas transmission studies on thin films are only able to partially resolve it, is due to two things: (i) the low quality of the internal crystal structure of thin films, and (ii) the fact that transmission studies on single crystals of reasonable thickness would not yield useful information because the strong optical activity associated with these four IR-allowed modes creates an opaque region, where fine structure would not be observable.

The appearance of quartets below the orientational-ordering transition is unexpected and not fully understood. In the perfectly ordered solid, the presence of a local crystal field splits each molecular F_{1u} vibration into $A_u + E_u + 3F_u$ modes in the solid. The A_u and E_u modes are not IR active, so that each F_{1u} mode may appear, at most, as three F_u modes. However, the presence of merohedral disorder implies that on average a least two nearest neighbors have the "wrong" orientations. The presence of disorder may do one of two things: (i) it may activate a silent A_u or E_u mode, or (ii) it may remove one of the degeneracies of a triply degenerate F_u mode. Thus, within a quartet, the three strong lines are most likely the F_u modes of the molecular F_{1u} mode, while the weaker feature is either the activation of a silent mode, or the splitting of one of the F_u modes due to disorder. Raman active modes have been observed to split in the orientationally ordered phase. However, in the LT phase the A_g, E_g, and F_g modes are all Raman active, yielding a large number of lines. In recent work[23,24] the number of observed lines is less than that predicted by group theory, making it impossible to gauge the effects of disorder.

The failure of the 576 cm^{-1} feature to display any indication of fine structure at low temperature is surprising, considering that this mode is primarily radial in nature[25,26] with a small tangential component, and all of the other F_{1u} modes (whether radial or tangential in nature) show clear splittings. An explanation has been previously proposed to explain why a given F_{1u} mode might not split, based on the nature of the degree of overlap between the 6:6 bond and the adjacent pentagon.[22] While this argument may have implications for vibrational coupling,[27] it is not related to the local crystal field, which is by definition a static distortion. For whatever reason, the 576 cm^{-1} feature is not affected by changes in the local crystal field.

In conclusion, we have shown here the high-resolution, infrared reflectance of undoped C_{60} single crystals, above and below the orientational-ordering transition, in the region of the four F_{1u} molecular (F_u) modes. At low temperature, three of the modes split into quartets, while the predominantly radial mode at ≈ 576 cm^{-1} shows no sign of fine structure or sensitivity to the changes in the local crystal field; this behavior is unaccounted for.

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