Effect of isotopic disorder on the $F_u$ modes in crystalline $C_{60}$

C. C. Homes, P. J. Horoyski, M. L. W. Thewalt, and B. P. Clayman

Department of Physics, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

T. R. Anthony
GE Corporate Research & Development Center, General Electric Company, Schenectady, New York 12301
(Received 17 July 1995)

The reflectance of undoped single-crystals of natural $C_{60}$ and isotopically pure $^{12}C_{60}$ and $^{13}C_{60}$ has been measured from 400 to 1600 cm$^{-1}$ at high resolution (0.2 cm$^{-1}$) above and below the orientational-ordering transition. In natural $C_{60}$, the $F_u(1)$ mode shows evidence for isotopic splitting at 295 K; all the other modes are singlets. Below the orientational-ordering transition the $F_u(1)$ mode splits into five resolvable components, the $F_u(3)$ and $F_u(4)$ modes split into quartets, and the $F_u(2)$ mode appears to remain a singlet. In the isotopically pure materials all the modes are singlets at 295 K; below the orientational-ordering transition, the $F_u(1)$ mode splits into only four components, the $F_u(3)$ and $F_u(4)$ modes split into triplets; the $F_u(2)$ mode shows only weak evidence for splitting. In those modes which display crystal-field splitting, isotopic disorder generates only a weak side band. The $F_u(1)$ mode displays fine structure which may be related to the intrinsic merohedral disorder in the ground state. It is proposed that the anomalous increase in the intermolecular strength of the $F_u(4)$ mode is due to a modulation of the charge density along the (110) intermolecular bonding directions.

I. INTRODUCTION

The discovery of an allotrope of carbon$^1$ in the form of a closed $C_{60}$ molecule (as well as a host of other geometries, collectively referred to as the “fullerenes”) and the recent discovery of an efficient form of synthesis$^2$ has generated a great deal of interest in the physical properties of this molecule and of molecular crystals composed of this unusual form of carbon.

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. Due to its exceptionally high point symmetry ($I_h$), the free $C_{60}$ molecule shows just 48 distinct vibrational modes. Only the four $F_{1u}$ modes are IR active, while the two $A_g$ and the eight $H_g$ modes are the only Raman active modes. Early IR measurements performed on $C_{60}$ films, KBr pellets, solutions and gas phase$^{3-4}$ revealed the four IR-active molecular $F_{1u}$ modes at $\approx 527$, $576$, $1183$, and $1429$ cm$^{-1}$. The first mid-IR transmission measurements on $C_{60}$ single crystals revealed that, in addition to the four $F_{1u}$ molecular modes (which become $F_u$ modes in the solid), there were many additional weaker lines.$^5$ These extra lines have been assigned mainly to second-order combination modes, as well as silent modes.$^6,7$ A detailed transmission study of the $F_u$ modes through the orientational-ordering transition in thin films showed the changes in linewidths of the $F_u(3)$ and $F_u(4)$ modes, as well as a splitting of the $F_u(4)$ mode.$^8$ More recent results, which rely on reflectance instead of transmission, show that the $F_u(1)$, $F_u(3)$, and $F_u(4)$ modes split into several components at low temperature,$^9,10$ while the $F_u(2)$ mode remains unsplit. Reflectance studies on single crystals are more useful than transmission studies for discerning fine structure for two reasons: (i) the internal crystal structure of thin films is poorer than that of single crystals, and (ii) the strong optical activity associated with the $F_u$ modes will create an opaque region in a film or crystal of any reasonable thickness, so that any fine structure would not be observable.

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 face-centered cubic lattice in an $Fm\overline{3}$ ($T_h^3$) space group, with four equivalent molecules, at $T_h$ symmetry sites, in the unit cell.$^{11}$ At room temperature, the molecules are orientationally disordered.$^{12}$ At $\approx 260$ K, the $C_{60}$ molecules undergo orientational ordering about any of four distinct (111) axes,$^{13}$ and simple cubic unit cell in a $Pn\overline{3}$ ($T_h^4$) space group is appropriate.$^{14}$ The molecules continue to undergo thermally activated reorientation until $\approx 90$ K, at which point these orientational jumps cease. However, the finite amount of static disorder existing at $\approx 90$ K is “frozen in” below this temperature. This disorder, initially thought to be random,$^{15}$ is usually discussed in terms of “merohedral disorder”$^{16}$ (which refers to the random site-by-site population of two different standard orientations$^{17}$). Despite the high density of “wrong” orientations (\% 17\%) at low temperature, there is still long-range orientational order in the low-temperature phase, and the average structure is still $Pa\overline{3}$. While the $C_{60}$ molecules are formal at $T_h$ sites, they are considered to possess $S_6$ site symme-
try. In a perfectly ordered ground state, the electron-rich bond between two hexagons (6:6) on one molecule points to an electron-deficient pentagonal ring on a neighboring molecule.\textsuperscript{14} Furthermore, the weak electrostatic repulsion of facing pentagons and 6:6 bonds along the (110) direction should lead to an increase in the electron density along the (100) direction, resulting in $S_6$ symmetry.

The factor-group analysis for both the high-temperature (HT) and perfectly ordered (but unobtainable) low-temperature (LT) phases has been previously determined.\textsuperscript{19} In the HT phase none of the IR-allowed $F_{1u}$ molecular modes are found 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 symmetry in both the HT and LT phases, there is no mixing of the IR and Raman modes.

Much of the fine structure observed in IR (Refs. 9 and 10) and Raman\textsuperscript{19–21} spectroscopy on crystalline C\textsubscript{60} have been ascribed to crystal-field splittings of the degenerate modes. However, it is also possible that isotopic disorder may result in the removal of degeneracies.\textsuperscript{22,23} Due to the 1.11\% natural abundance of $^{13}$C, almost half of all naturally occurring C\textsubscript{60} molecules have one or more substitutions of $^{13}$C for $^{12}$C ($\approx 34\%$ $^{13}$C\textsubscript{12}C\textsubscript{59}, $\approx 15\%$ have two or more $^{13}$C atoms per molecule\textsuperscript{24}); such isotopic splittings have recently been observed for the $A_g(2)$ mode of isolated natural C\textsubscript{60} molecules in frozen CS\textsubscript{2}.\textsuperscript{25}

To study the effects of isotopic disorder on the molecular $F_{1u}$ modes in crystalline C\textsubscript{60}, the high-resolution reflectance of crystalline C\textsubscript{60} and isotopically pure crystalline $^{12}$C\textsubscript{60} and $^{13}$C\textsubscript{60} was measured at 295 K, and at 10 K in the orientationally ordered ground state. A comparison of these results indicates that in general, the presence of isotopic disorder introduces only weak fine structure into the molecular $F_{1u}$ modes in the solid, and that the majority of the fine structure is due to the crystal field, and the concomitant merohedral disorder. The $F_u(1)$ and $F_u(2)$ modes are exceptions. The $F_u(1)$ mode, which appears to display isotopic splitting in the disordered state at room temperature, undergoes a substantial reorganization of the vibrational energy in the orientationally ordered ground state in the presence of isotopic disorder. The $F_u(2)$ mode fails to show any evidence of isotopic splitting, and only weak evidence of crystal-field splitting.

**II. EXPERIMENTAL DETAILS**

The samples were prepared from C\textsubscript{60} powder (Texas Fullerenes), which had a C\textsubscript{60} purity of 99.9\% (in terms of other fullerenes). Single crystals of volumes from 0.1 to $>1$ mm$^3$ were grown by sublimation in a temperature gradient under vacuum in quartz tubes,\textsuperscript{26} after outgassing the powder at 250°C. The single crystals of $^{12}$C\textsubscript{60} and $^{13}$C\textsubscript{60} were similarly grown from $^{12}$C\textsubscript{60} powder produced in the usual manner\textsuperscript{27} from pyrolytic graphite rods deposited from 99.95\% $^{12}$C and 99.7\% $^{13}$C methane (Cambridge Isotope Labs). Mass spectroscopy revealed the expected 51\% concentration of $^{12}$C\textsubscript{60} in the natural material, and 97.3\% $^{12}$C\textsubscript{60} in the “pure” sample consistent with the 99.95\% $^{12}$C content of the methane. The slightly lower purity of the $^{13}$C methane leads to $\approx 85\%$ concentration of $^{13}$C\textsubscript{60} molecules.

The resulting crystals were highly faceted, with irregular back surfaces. The typical dimensions of one of the trapezoidal facets was typically less than a millimeter along any given side. The samples were mounted on optically black cones, and the absolute reflectance was then measured using an in situ overcoating technique\textsuperscript{27} on a Bruker IFS 113V Fourier transform interferometer from 400 to 1600 cm$^{-1}$, at a resolution of 0.2 cm$^{-1}$. Due to the small size of the samples, below 700 cm$^{-1}$, a liquid helium bolometer was used, while in the mid-infrared a liquid nitrogen MCT (HgCdTe, or mercury cadmium tellurium) detector was employed. The measured absolute reflectance has an estimated accuracy of $\pm 1\%$.

**III. RESULTS**

The reflectance of the $F_u(1)$ and $F_u(2)$ modes, obtained from natural crystalline C\textsubscript{60}, as well as isotopically pure crystalline $^{12}$C\textsubscript{60} and $^{13}$C\textsubscript{60}, are shown in Figs. 1(a)–(c) and Figs. 1(d)–(f), respectively. The reflectance of the $F_u(3)$ and $F_u(4)$ modes, obtained from natural crystalline C\textsubscript{60}, as well as isotopically pure crystalline $^{12}$C\textsubscript{60} and $^{13}$C\textsubscript{60}, are shown in Figs. 2(a)–(c) and Figs. 2(d)–(f), respectively. The line shapes in the reflectance have been fitted to one or more Lorentzian oscillators with

$$\tilde{\epsilon}(\omega) = \epsilon_\infty + \sum_j \frac{\omega_{pj}^2}{\omega_j^2 - \omega^2 - i\omega\gamma_j},$$  \hspace{1cm} (1)

where $\tilde{\epsilon} = \epsilon_1 + i\epsilon_2$ is the complex dielectric function, $\epsilon_\infty$ is a constant term, and $\omega_j$, $\gamma_j$, and $\omega_{pj}$ are the frequency, width, and effective plasma frequency of the $j$th vibration. The real and imaginary parts of the refractive index $n = n + ik$ are

$$n = \left[ \frac{1}{2} \left( \sqrt{\epsilon_1^2 + \epsilon_2^2 + \epsilon_1} \right) \right]^{1/2},$$  \hspace{1cm} (2)

and

$$k = \left[ \frac{1}{2} \left( \sqrt{\epsilon_1^2 + \epsilon_2^2 - \epsilon_1} \right) \right]^{1/2},$$  \hspace{1cm} (3)

from which the reflectance ($R$) is calculated,

$$R = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2}.$$  \hspace{1cm} (4)

The results of the fits to the four $F_u$ modes for natural crystalline C\textsubscript{60}, as well as the isotopically pure $^{12}$C\textsubscript{60} and $^{13}$C\textsubscript{60} materials at 295 K and 10 K are shown in Tables I and II, respectively. In each of the fits, the value returned for $\epsilon_\infty \approx 4$, in good agreement with ellipsometry measurements on thin films below the band edge.\textsuperscript{28} The fitted values for the fundamental frequencies at 10 K are indicated by the downward pointing arrows in the plots.
of the reflectance in Figs. 1 and 2. The uncertainties in the values returned by the fits are estimated to be less than ±0.04 cm⁻¹ for ω₁, and less than ±4% in γ₁ and ωₚ₁. In broad or weak modes, these uncertainties will tend to be larger.

The detailed temperature dependence of the Ĥ₁(1) mode has been studied in ¹²C₆₀, and is shown in Fig. 3(a) as a function of temperature. Below the orientational-ordering transition the line shape first displays an asymmetry, then splits into a triplet. The arrows in Fig. 3(a) refer to the fitted frequencies determined from the reflectance at 10 K. The optical conductivity has been calculated from the reflectance curves in Fig. 3(a), using a Hilbert transform, and is shown in Fig. 3(b). Because high- and low-frequency extrapolations are required for the Hilbert transform, there is some uncertainty as to the absolute value of the conductivity. While the reflectance is a combination of the real and imaginary parts of ε(ω), the optical conductivity σ(ω) depends only on the imaginary part of the dielectric function, [σ(ω) = ε₂(ω)/4π], which is in turn proportional to the absorption. It is important to note that the frequencies fit, using the reflectance data, agree quite well with the peaks in the conductivity at 526.02 cm⁻¹ and 527.56 cm⁻¹; the 526.47 cm⁻¹ mode lies too close to the much stronger 526.02 cm⁻¹ vibration to be clearly resolved.

IV. DISCUSSION

The effect of ¹³C substitution into a C₆₀ molecule may be naïvely modeled using a simple harmonic model with ω/ω₀ = √[m₁/2m]; where m₁ is the reduced mass of ¹²C₆₀, m is the reduced mass of the C₆₀ molecule containing ¹³C substitutions, and ω₀ and ω are the unperturbed and the perturbed frequencies, respectively. Using the room temperature values for the Ĥ₁(1, 2, 3, 4) modes in ¹²C₆₀ the predicted isotope shifts in natural C₆₀ (with a single ¹³C atom) are 0.34, 0.37, 0.76 and 0.92 cm⁻¹, respectively. The isotopic perturbations have also been calculated from an ab initio model by Weeks;²² within the framework of this model, more detail is revealed as each mode is split into a triplet with a weakly perturbed fundamental and two vibrations activated by isotopic disorder. By examining only shifts of greater than 0.1 cm⁻¹, the ab initio model yields shifts for the Ĥ₁(1, 2) modes of 0.45 and 1.15 cm⁻¹, respectively, for the Ĥ₁(3) mode shifts of 0.96 and 1.50 cm⁻¹, and for the Ĥ₁(4) mode shifts of 1.72 and 2.37 cm⁻¹ — these shifts are larger than those predicted by the simple harmonic model.

At 295 K, the Ĥ₁(1) mode in natural crystalline C₆₀ shown in Fig. 1(a) is a doublet, while the same feature in ¹²C₆₀ and ¹³C₆₀, shown in Figs. 1(b) and 1(c), is a sin-

FIG. 1. The reflectance of the Ĥ₁(1) mode at 295 K and 10 K in (a) natural C₆₀, (b) ¹²C₆₀, and (c) ¹³C₆₀. The reflectance of the Ĥ₁(2) mode at 295 K and 10 K in (c) natural C₆₀, (d) ¹²C₆₀, and (e) ¹³C₆₀. The resolution is 0.2 cm⁻¹ for all measurements. The arrows indicate the positions of the fitted frequencies at 10 K (see Table II). At 295 K, the Ĥ₁(1) mode is split into a doublet in the natural material, but it is observed to be a singlet in the isotopically pure materials; the Ĥ₁(2) mode is observed as a singlet. Below the orientational-ordering transition, the Ĥ₁(1) mode splits into five components in the natural material, but only four components in both of the isotopically pure materials; the Ĥ₁(2) mode fails to show any sign of isotopic splitting, and only weak evidence for crystal-field splitting.
glet. The doublet splitting at room temperature of this mode in the natural crystalline material has been observed in samples from several different crystal growths. The strongest component of the \( F_{u}(1) \) mode in the natural \( C_{60} \) at 526.70 cm\(^{-1}\) is close to the mode in \(^{12}\)\(C_{60}\) at 526.53 cm\(^{-1}\). Originally, the doublet structure of the \( F_{u}(1) \) mode in the natural material was taken as an indication of the crystal lattice imposing some degree of preferential orientation on the molecules.\(^9\) However, the results from the isotopically pure materials indicate that this splitting arises as a consequence of isotopic disorder. This interpretation is complicated by the fact that the observed splitting of \( \approx 1 \) cm\(^{-1}\) is much larger than the shifts predicted by either of the models by almost a factor of 2.

At 10 K, the \( F_{u}(1) \) mode splits into four strong com-

![Image of a graph with multiple plots labeled (a) \( F_{u}(3) \) \( C_{60} \) at 295 K and 10 K, (b) \( F_{u}(3) \) \(^{12}\)\(C_{60}\) at 295 K and 10 K, (c) \( F_{u}(3) \) \(^{12}\)\(C_{60}\) at 295 K and 10 K, (d) \( F_{u}(4) \) \( C_{60} \) at 295 K and 10 K, (e) \( F_{u}(4) \) \(^{12}\)\(C_{60}\) at 295 K and 10 K, and (f) \( F_{u}(4) \) \(^{12}\)\(C_{60}\) at 295 K and 10 K. The reflectance of the \( F_{u}(4) \) mode at 295 K and 10 K in (a) natural \( C_{60} \), (b) \(^{12}\)\(C_{60}\), and (c) \(^{12}\)\(C_{60}\). The reflectance of the \( F_{u}(4) \) mode at 295 K and 10 K in (c) natural \( C_{60} \), (d) \(^{12}\)\(C_{60}\), and (e) \(^{12}\)\(C_{60}\). The resolution is 0.2 cm\(^{-1}\) for all measurements. The arrows indicate the positions of the fitted frequencies at 10 K (see Table II). At 295 K, both the \( F_{u}(3) \) and \( F_{u}(4) \) modes are single. Below the orientational-ordering transition, the \( F_{u}(3) \) and \( F_{u}(4) \) modes both split into four components in the natural material, but only three components in the isotopically pure materials.

TABLE I. The fitted parameters for the vibrational features for the four infrared-active \( F_{u} \) modes in crystalline natural \( C_{60} \), and isotopically pure \(^{12}\)\(C_{60}\) and \(^{12}\)\(C_{60}\) at room temperature. The features that have been identified as due to isotopic disorder have been indicated by an asterisk (*). (All units are in cm\(^{-1}\).)

<table>
<thead>
<tr>
<th></th>
<th>(^{12})(C_{60})</th>
<th>( C_{60} )</th>
<th>(^{13})(C_{60})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \omega_{i} )</td>
<td>1.56</td>
<td>93</td>
<td>1.68</td>
</tr>
<tr>
<td>( \gamma_{i} )</td>
<td>526.53</td>
<td></td>
<td>525.67</td>
</tr>
<tr>
<td>( \omega_{pl} )</td>
<td></td>
<td></td>
<td>576.08</td>
</tr>
<tr>
<td>( \omega_{pl} )</td>
<td>1183.58</td>
<td>2.05</td>
<td>50</td>
</tr>
<tr>
<td>( \omega_{pl} )</td>
<td>1429.73</td>
<td>3.15</td>
<td>53</td>
</tr>
</tbody>
</table>

\(^{a}\)The value of \( \epsilon_{\infty} \approx 4 \) returned from the fits is in good agreement with the values for \( \epsilon_{i} \) below the band gap as measured by ellipsometry on \( C_{60} \) films [after Kelly et al., Phys. Rev. B 46, 4693 (1992)].
TABLE II. The fitted parameters* for the vibrational features for the four infrared-active \( F_u \) modes in crystalline natural \( C_{60} \), and isotopically pure \( ^{12}C_{60} \) and \( ^{13}C_{60} \) at 10 K. The resolution of the fitted spectra was 0.2 cm\(^{-1}\). The features that have been identified as due to isotopic disorder have been indicated by an asterisk (*). (All units are in cm\(^{-1}\).)

<table>
<thead>
<tr>
<th>( ^{12}C_{60} )</th>
<th>( ^{13}C_{60} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \omega_i )</td>
<td>( \gamma_i )</td>
</tr>
<tr>
<td>526.02</td>
<td>0.36</td>
</tr>
<tr>
<td>526.47</td>
<td>0.34</td>
</tr>
<tr>
<td>527.56</td>
<td>0.29</td>
</tr>
<tr>
<td>529.37</td>
<td>0.34</td>
</tr>
<tr>
<td>529.28</td>
<td>0.48</td>
</tr>
<tr>
<td>576.72</td>
<td>0.11b</td>
</tr>
<tr>
<td>1181.88</td>
<td>0.38</td>
</tr>
<tr>
<td>1183.86</td>
<td>0.41</td>
</tr>
<tr>
<td>1184.57</td>
<td>0.74</td>
</tr>
<tr>
<td>1428.55</td>
<td>0.33</td>
</tr>
<tr>
<td>1430.80</td>
<td>0.50</td>
</tr>
<tr>
<td>1432.41</td>
<td>1.37</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*The value of \( \epsilon_\infty \approx 4 \) returned from the fits is in good agreement with the values for \( \epsilon_1 \) below the band gap as measured by ellipsometry on \( C_{60} \) films [after Kelly et al., Phys. Rev. B 46, 4693 (1992)].

b Spectra obtained using a resolution of 0.1 cm\(^{-1}\) yielded a width of 0.08 cm\(^{-1}\), suggesting that the width of this line is not fully resolved.

Components, accompanied by a very weak mode at slightly higher frequency, as indicated by the arrows in Fig. 1(a). In the isotopically pure \( ^{12}C_{60} \) and \( ^{13}C_{60} \) materials at 10 K, shown in Figs. 1(b) and 1(c), the \( F_u(1) \) mode has split into only three components, but the weak mode at slightly higher frequency is still observed, indicating that the weak feature at 525.28 cm\(^{-1}\) in the natural material is caused by isotopic disorder; the splitting of 0.48 cm\(^{-1}\) between this mode and the fundamental mode is in excellent agreement with the \( ab \) initio prediction of 0.45 cm\(^{-1}\), and is only somewhat larger than the shift of 0.34 cm\(^{-1}\) predicted by the simple harmonic model. The difference in the size of the isotope splitting above and below the orientational-ordering transition is unexpected, and creates some uncertainty as to whether or not the doublet observed at room temperature is due strictly to isotopic effects.

The isotopic substitution of a single \( ^{13}C \) atom into a \( ^{12}C_{60} \) molecule (\( ^{12}C_{60}{^{13}C} \)) leads to a reduction in the molecular symmetry (\( \tilde{f}_h \rightarrow C_{2h} \)), and has the potential to split each \( F_u \) mode into a triplet. Successive substitutions (\( ^{13}C_3^{12}C_{58} \), etc.) will reduce the symmetry of the molecule even more, and lead to further splitting. Thus, each mode that is associated with crystal-field splitting in the isotopically pure systems should have at least two features associated with it in the natural material. However, the modes generated by the crystal-field splitting are much weaker than the fundamental, and the modes due to isotopic disorder associated with these features may be either too weak to observe, or may be superimposed on much stronger features and remain unresolved. Thus, it is not entirely surprising that we only observe a single mode attributed to isotopic disorder, and that this mode is associated with the strongest vibration.

The very weak feature observed \( \approx 2 \) cm\(^{-1}\) above the strong features associated with the \( F_u(1) \) fundamental is nearly an order of magnitude weaker than the features fitted in the reflectance — this feature is also present in the isotopically pure systems, indicating that it is due to the crystal field. In the perfectly ordered ground state in the isotopically pure systems, the \( F_u(1) \) mode would be expected to split into a triplet at most. However, the presence of merohedral disorder may activate the silent \( A_g \) or \( E_u \) modes, or remove one of the degeneracies of a triply degenerate \( F_u \) mode. The total oscillator strength of the \( F_u(1) \) mode (which is \( \propto \sum \omega_{pi}^2 \), where \( i \) indexes the vibrational components associated with an observed splitting) is roughly constant in the three materials, both above and below the orientational-ordering transition. However, while the distribution of oscillator strength in crystalline \( ^{12}C_{60} \) and \( ^{13}C_{60} \) is nearly identical, the presence of isotopic disorder leads to a major redistribution of oscillator strength in the natural material. This redistribution may arise in one of two ways. If the origin is internal, then this suggests that isotopic substitution changes the nature of the vibration(s) in a fundamental way. However, such a change is usually accompanied by a shift in frequency, and there is indeed a 0.26 cm\(^{-1}\) shift in the frequency of the \( F_u(1) \) fundamental in natural \( C_{60} \) and \( ^{12}C_{60} \) material at 10 K (0.17 cm\(^{-1}\) at room temperature). However, the small size of the frequency shift makes it unlikely that simple isotopic disorder is respon-
sible for such a large redistribution of oscillator strength. This leaves the possibility that this effect is due to external factors, such as intermolecular vibrational coupling, or band structure effects. This possibility has been proposed to explain the unusual Raman frequency shifts in the natural and isotopically pure materials for the $A_g(2)$ mode.\textsuperscript{21}

The $F_u(2)$ mode is a singlet in both the natural and isotopically pure crystalline materials at room temperature. Below the orientational-ordering transition, the $F_u(2)$ mode shows no obvious signs of splitting in the natural C$_{60}$, shown in Fig. 1(d). However, there is an extremely weak feature seen $\approx 1$ cm$^{-1}$ below the strong fundamental [visible in both Figs. 1(e) and 1(f)]; the fact this weak feature is observed in the isotopically pure materials indicates it is likely due to crystal-field effects.

While there is no obvious splitting due to isotopic disorder in the $F_u(2)$ mode, the frequency of the fundamental in natural C$_{60}$ and $^{12}$C$_{60}$ is observed to shift by 0.17 cm$^{-1}$ and 0.33 cm$^{-1}$ at room temperature and 10 K, respectively. This is an unexpected result. The observation of a shift between natural C$_{60}$ and $^{12}$C$_{60}$, but no isotopic splitting in the natural material, suggests that the $F_u(2)$ mode is behaving as if the C$_{60}$ molecules possess an average molecular weight in the natural material. This behavior has also been observed in a detailed study of the effects of isotopic disorder on the Raman modes,\textsuperscript{31} and suggests that there may be enough intermolecular vibrational coupling present so that the observed frequency of the $F_u(2)$ mode in the natural material is an ensemble average, rather than the discrete vibrations of separate molecules. While the frequency of the mode will be given by the average mass of the molecules, the variation in the masses of the individual molecules will lead to line broadening in the isotopically disordered material. At 10 K, the linewidth in the natural material is indeed nearly twice that observed for pure $^{12}$C$_{60}$. The linewidth of the $F_u(2)$ mode has been observed to narrow discontinuously at the orientational-ordering transition.\textsuperscript{10} In the isotopically pure materials, the $F_u(2)$ linewidth narrows by over an order of magnitude from 1.56 cm$^{-1}$ at 295 K to 0.11 cm$^{-1}$ at 10 K. An additional experiment performed at a resolution of 0.1 cm$^{-1}$ allowed the line shape to be fitted with a width of 0.08 cm$^{-1}$; even at this high resolution, it is not clear that the width of this mode has been fully resolved.

It is worthwhile to point out that one of the advantages of reflectance over transmission measurements not previously discussed is in fitting line shapes. To illustrate this point, the panels in Fig. 4 show the real and imaginary parts of $\hat{e}(\omega)$ and $\hat{n}(\omega)$, and the reflectance for a Lorentzian oscillator with $\omega_0 = 576$ cm$^{-1}$, $\gamma_0 = 0.1$ cm$^{-1}$, $\omega_\infty = 50$ cm$^{-1}$, and $\epsilon_\infty = 4$. The absorption, which is related to the imaginary part of the dielectric function [shown in Fig. 4(b)], has a full width at half maximum of 0.1 cm$^{-1}$ — thus, resolutions higher than 0.1 cm$^{-1}$ will be required to properly resolve this line shape in transmission. On the other hand, the dispersive shape of $\epsilon_\infty$ and $\hat{n}$ [shown in Fig. 4(a)] can be observed to vary over nearly 1 cm$^{-1}$ ($k$ is also quite broad), so that the reflectance shown in Fig. 4(c) displays a rather broad line shape, despite the fact that $\gamma_0 = 0.1$ cm$^{-1}$. The reflectance for $\gamma_0 = 0.2$ cm$^{-1}$ and 0.4 cm$^{-1}$ are also shown in Fig. 4(c). Increasing the linewidth has the effect of decreasing the amplitude of the reflectance, while only slightly broadening the feature, indicating that it is the overall shape of the line which must be considered in any determination of the width. Thus, dispersive line shapes measured in reflectance can often yield linewidths that are less than the quoted instrumental resolution, as is the case in this work for the $F_u(2)$ mode.

The two low-frequency $F_u(1)$ and $F_u(2)$ vibrations involve predominantly radial displacements.\textsuperscript{32} In contrast, the much weaker $F_u(3)$ and $F_u(4)$ modes are mainly tangential in nature. The $F_u(3)$ mode appears as a singlet at 295 K in the natural and isotopically pure crystalline materials. In the natural material, the $F_u(3)$ mode splits into four resolvable components at 10 K, while in the isotopically pure materials, it is only observed to split into three components. This suggests that the presence of isotopic disorder is responsible for the weak mode at 1182.83 cm$^{-1}$ in natural C$_{60}$; the splitting between this mode and
the fundamental in the natural material is close to the expected value of \( \approx 0.8 \text{ cm}^{-1} \) predicted by the simple harmonic model. While the weakest component of the \( F_u(3) \) mode is difficult to separate from the background noise in the reflectance, attempts to reproduce the overall reflectance line shape fail unless a mode just below the fundamental is included.

At 295 K, the \( F_u(4) \) mode is a singlet in the natural and isotopically pure crystalline materials. In natural \( C_{60} \), the \( F_u(4) \) mode splits into four components at 10 K. However, in the isotopically pure materials, the \( F_u(4) \) mode is observed to split into only a triplet. This suggests that the weak mode at 1427.56 cm\(^{-1}\) in the natural material is due to isotopic disorder; the position of this feature \( \approx 1 \text{ cm}^{-1} \) below a strong, sharp feature is in good agreement with the splitting of \( \approx 0.9 \text{ cm}^{-1} \) predicted by the simple harmonic model, but is significantly less than the splittings predicted by the \( ab\ initio \) model. In general, the lower values predicted for the isotopic shifts predicted by the simple harmonic model are in better agreement with the data than those predicted by the \( ab\ initio \) calculations.

There is an extremely weak feature at \( \approx 1425 \text{ cm}^{-1} \) in the natural material; this feature is also present in crystalline \( ^{12}\text{C}_{60} \), indicating that it does not arise from isotopic disorder. This feature has also been observed in thin films above and below the orientational-ordering transition, and has recently been assigned to the \( H_g(7) \) mode, suggesting perhaps that some of the molecules in the solid do not possess an inversion symmetry.

With the exception of the frequency shifts, the line shapes of the \( F_u \) modes in crystalline \( ^{12}\text{C}_{60} \) are essentially identical to those observed in crystalline \( ^{13}\text{C}_{60} \) (despite its lower purity). The ratio of the \( \omega/\omega_0 \) for \( ^{12}\text{C}_{60} \) to \( ^{13}\text{C}_{60} \), based purely on the mass change in a simple harmonic oscillator, is expected to be \( \approx 0.9608 \). In each case, the observed ratio falls in the range 0.9612 \( \rightarrow \) 0.9617, which although slightly above the predicted value is nonetheless in excellent agreement. This is an indication that the nature of the vibrations in the two isotopically pure systems has not been altered by the change in mass.

In both the natural and isotopically pure materials, the \( F_u(4) \) mode displays an unusual feature that is not observed in any of the other infrared active \( F_u \) modes, namely, an anomalous increase in the total oscillator strength below the orientational-ordering transition. For each of the first three \( F_u \) modes, the total oscillator strength is essentially the same above and below the orientational-ordering transition. However, in the case of the \( F_u(4) \) mode, the oscillator strength increases by \( \approx 60\% \).

As previously mentioned, in the perfectly ordered ground state, the 6:6 bond (between two hexagons) has a significant \( \pi \)-electron density, and faces an electron-deficient pentagonal ring on a neighboring molecule, as shown in Fig. 5. The exceptionally high symmetry of the \( C_{60} \) molecule allows this condition to be satisfied for all twelve nearest neighbors. It is this high degree of bonding optimization that stabilizes the ordered phase. It is well known that the formal charge associated with a carbon double bond is very sensitive to the bond length. Thus, as the 6:6 bond undergoes compression and elongation, the charge associated with this bond increases and decreases, respectively. Allowing that the molecules in

![FIG. 4. The (a) real and (b) imaginary parts of \( \epsilon(\omega) \) oscillator with \( \omega_0 = 576 \text{ cm}^{-1} \), \( \gamma_0 = 0.1 \text{ cm}^{-1} \), \( \omega_\text{p0} = 50 \text{ cm}^{-1} \), and \( \epsilon_\infty = 4 \), after Eqs. (1) – (4). (c) The reflectance for a Lorentzian oscillator with the same parameters as above (solid line), as well as for \( \gamma_0 = 0.2 \text{ cm}^{-1} \) (dotted line) and \( \gamma_0 = 0.4 \text{ cm}^{-1} \) (dash-dot line). The arrow refers to the position of \( \omega_0 \). Note that the dispersive line shape of the reflectance is much broader than the imaginary part of the dielectric function, even though the linewidth is the same for both functions.](image)

![FIG. 5. The projection along the intermolecular axis. The arrows indicate the primarily tangential atomic displacements of the \( F_u(4) \) mode. The dashed line indicates the electron-rich bond between two hexagons (6:6), which is adjacent to an electron-deficient pentagonal ring on a neighboring molecule in the orientationally ordered phase. As the 6:6 bond undergoes an elongation and compression, and the pentagon undergoes compression and rarefaction, in the plane of the paper.](image)
the solid vibrate in phase, then at the same time the 6:6 bond is undergoing compression (increase in charge), the neighboring electron-deficient pentagonal ring is undergoing rarefaction (decrease in charge). In this way, the modulation of the charge density along the intermolecular bonding directions forms an IR-active dipole moment, which vibrates at the same frequency as the $F_n(4)$ mode, leading to enhancement of the oscillator strength in the orientationally ordered phase.

This mechanism is similar to the charge-transfer (CT) coupling observed in molecular clusters and linear chain materials, where the oscillator strengths of certain symmetry species of molecular vibrations are observed to be dramatically enhanced. However, CT coupling requires a significant amount of overlap between molecular orbitals, so that a dipole moment is formed by the charge being pumped from one molecule to another. The weak electrostatic bonding in C$_{60}$ does not involve any significant orbital overlap.

V. CONCLUSIONS

The reflectance in the region of the four IR-active $F_n$ modes ($F_{1n}$ molecular) has been measured at a high resolution (0.2 cm$^{-1}$) above and below the orientational-ordering transition in natural and isotopically pure crystalline C$_{60}$. At 295 K, the only mode that appears to undergo isotopic splitting in natural crystalline C$_{60}$ is the $F_n(1)$ mode; all the other modes appear as singlets at room temperature. In the natural material, below the orientational-ordering transition, the $F_n(1)$ mode splits into five resolvable components, and the $F_n(3)$ and $F_n(4)$ modes split into triplets. In the isotopically pure materials, the $F_n(1)$ mode splits into a quartet, and the $F_n(3)$ and $F_n(4)$ modes only split into triplets, indicating that isotopic disorder is responsible only for weak structure, and will typically only be associated with a strong fundamental. The $F_n(2)$ mode, while broader in the orientationally ordered phase in the natural material than in the isotopically pure materials, shows no signs of isotopic splitting, and only very weak evidence of crystal-field splitting. In general, the observed isotope shifts are in good agreement with the values predicted by a simple harmonic model.

The presence of more than three components of the $F_n(1)$ mode in the low-temperature phase of the isotopically pure materials is attributed to the presence of merohedral disorder. The major redistribution of oscillator strength that occurs in the $F_n(1)$ mode from the isotopically pure to natural crystalline C$_{60}$ suggests that the isotopic disorder may be interacting with band structure effects. The two low-frequency radial modes display isotope-induced shifts of the fundamentals, suggesting intermolecular vibrational coupling. It is proposed that the anomalous increase in oscillator strength of the $F_n(4)$ mode below the orientational-ordering transition is due to the modulation of the charge density along the intermolecular bonding directions.

ACKNOWLEDGMENTS

We are grateful to A.W. McConnell for assistance in the laboratory. We are indebted to Cambridge Isotope Labs for assistance in obtaining the $^{12}$C and $^{13}$C enriched methane. This work was supported by the Natural Sciences and Engineering Research Council of Canada and Simon Fraser University.

The integrated area for a Lorentzian oscillator, the second term in Eq. (1), is simply \( \omega_j^2 / 8 \), independent of the values for \( \omega_j \) and \( \gamma_j \), so that for a group of oscillators, the total integrated strength \( \propto \sum_j \omega_{pj}^2 \).