# Observation of higher-order infrared modes in solid $C_{60}$ films

K.-A. Wang, A. M. Rao, and P. C. Eklund
*Department of Physics & Astronomy and Center for Applied Energy Research, University of Kentucky, Lexington, Kentucky 40506*

M. S. Dresselhaus
*Department of Electrical Engineering & Computer Science and Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

G. Dresselhaus
*Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*
(Received 1 June 1993)

In this paper, we present a rich (4 strong $F_{1u}$ first-order and an additional 98 weak lines) ir spectrum for a 4-$\mu$m-thick $C_{60}$ film on KBr in the range 400–4000 $cm^{-1}$. Most of the weak lines are identified with second-order combination modes. More accurate frequencies of some optically inactive modes in $C_{60}$ have been obtained by simultaneously analyzing the higher-order ir and Raman spectra. Isotope-induced symmetry lowering in $C_{60}$ molecules has also been observed and is responsible for activating several fundamental modes which would otherwise be ir inactive.

Solid $C_{60}$ is a nearly ideal molecular solid with ten $(2A_g+8H_g)$ Raman-active and four $(F_{1u})$ ir-active modes,[1,2] consistent with group-theoretical predictions for an isolated $C_{60}$ molecule with icosahedral $(I_h)$ symmetry.[1,3] Out of the $174(=180-6)$ intramolecular vibrational modes in an icosahedal $C_{60}$ molecule, only 46 distinct mode frequencies are possible.[1,3] Some of these modes have been determined experimentally by first-order Raman and infrared (ir) spectroscopy,[1,2,4] high-resolution electron-energy-loss spectroscopy (HREELS),[5] photoluminescence (PL),[6] and neutron inelastic-scattering (NIS) experiments.[7] Of these various methods, the Raman and ir spectroscopies provide detailed information about mode symmetries, and the inherent high resolution affords a more accurate determination of the mode frequencies. Recently, we reported the observation and interpretation of numerous higher-order Raman features in solid $C_{60}$ at temperatures well above and below the orientational ordering transition.[8] This prior Raman study in solid $C_{60}$ led us to conclude that most of the additional sharp features observed below 1600 $cm^{-1}$ should be assigned to higher-order intramolecular scattering or to the isotopic activation of otherwise silent intramolecular modes,[8] rather than to first-order scattering from otherwise Raman-silent modes activated by solid-state crystal-field effects.[9] Consistent with the ir spectrum reported here, the sharpness of the observed second-order Raman features[8] was taken as further important evidence that phonon dispersion in the solid state is very weak, supporting the picture of the nearly ideal molecular nature of solid $C_{60}$.

In this paper we report the observation of numerous higher-order sharp features in the ir spectrum of a thin film of solid $C_{60}$. Beside the four first-order-allowed $(F_{1u})$ ir modes, at least 98 additional weak lines are observed in the 400–4000 $cm^{-1}$ frequency range, many of which are tentatively identified with second-order combination modes, as discussed in greater detail below. Meanwhile, several of the weak lines are identified with first-order modes which would *not* be ir active in an isotopically pure $C_{60}$ molecule, but are proposed here to be activated by the isotopic substitution of naturally abundant $^{13}C$. From an analysis of the data, we are able to obtain values for many silent mode frequencies, which are found to be in good agreement with those obtained previously from analysis of the higher-order Raman spectrum.[8] In addition to the four $F_{1u}$ modes, Chase, Herron, and Holler[10] also reported numerous other weak features in their ir spectrum for a thick $(d=14\ \mu m)$ solid $C_{60}$ film. Although they discussed combination modes as a possible origin of the many weak lines in the spectrum, they did not make any specific assignments.

High-purity (99.7%) microcrystalline $C_{60}$ power was first loaded into a quartz tube and degassed at 250 °C under a dynamic vacuum $3\times10^{-5}$ Torr for $\sim$6 h in order to remove any residual solvent (mostly toluene). Details for the extraction and purification of $C_{60}$ can be found in our previous publications.[1] The heat-treated powder was then transferred into a molybdenum boat inside a film deposition chamber that is housed inside a glove box (helium atmosphere; $O_2$,$H_2O$ $<1$ ppm). *In situ* preheating the $C_{60}$ power for $\sim$15 min. was further carried out to minimize the amount of toluene impurity in the films. A sufficiently thick $(d\approx4\ \mu m)$ $C_{60}$ film was deposited onto a KBr substrate (1.0-in. diam, $\frac{1}{8}$-in. thickness) in order to discern the weak higher-order and other spectral features in the ir transmission spectrum of solid $C_{60}$. The $T=300$ K transmission spectrum was recorded with 1 $cm^{-1}$ resolution in a nitrogen purged Digilab FTS 80 Fourier-transform spectrometer equipped with a germanium-coated KBr beamsplitter and a triglycine sulfate (TGS) detector.

 

Figure 1(a) shows the near-normal incidence, room-temperature ir transmission spectrum for the $C_{60}$ film on KBr in the frequency range 400–4000 $cm^{-1}$. Figures 1(b) and 1(c) show, accordingly, the lower- and higher-frequency portions of the same spectrum on an expanded scale to allow better observation of the weak sharp features. Narrow structures associated with various first- and higher-order vibrational modes are superimposed on

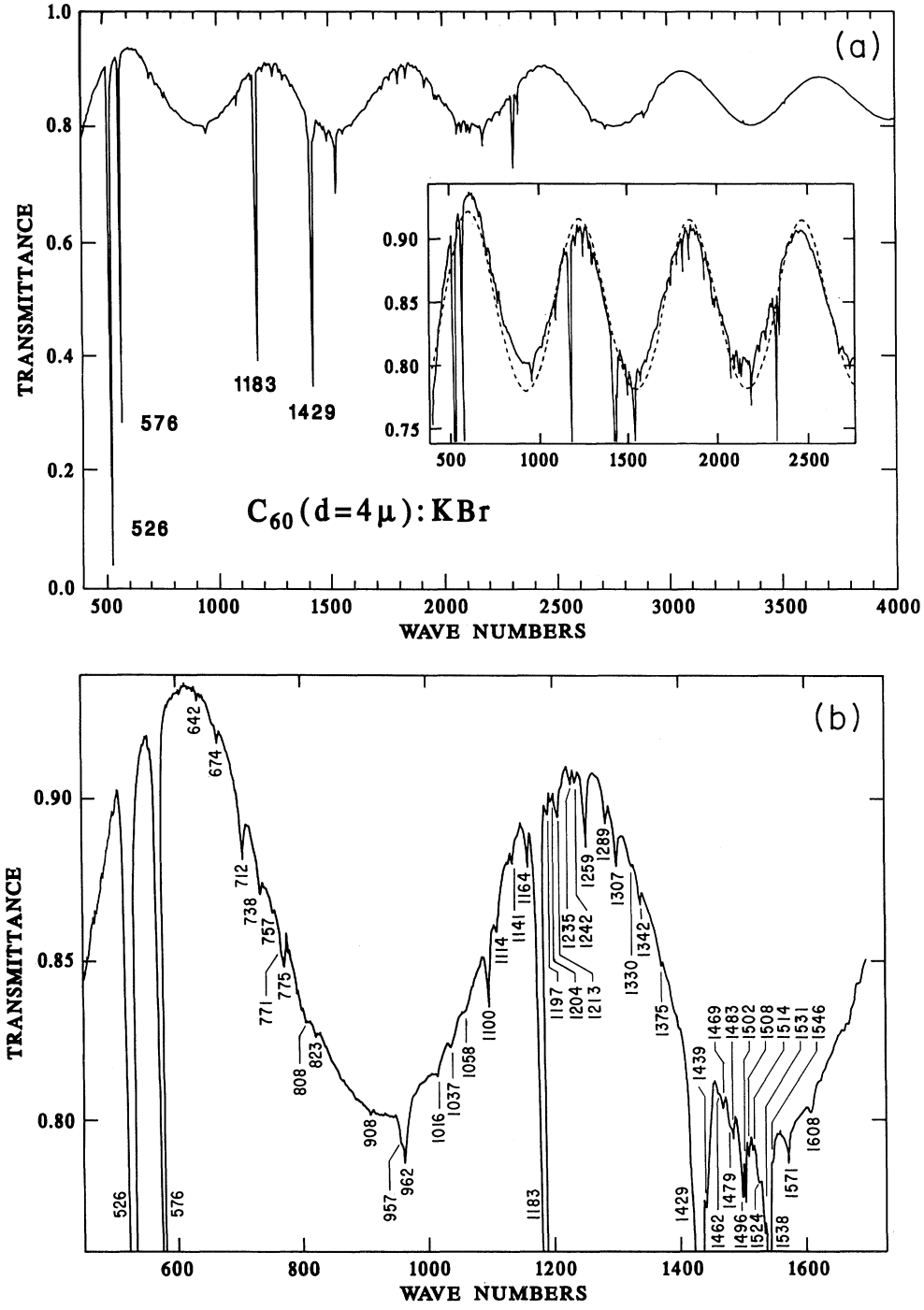


FIG. 1. (a) Infrared transmission (400–4000 $cm^{-1}$) spectrum ($T=300$ K) of a $C_{60}$ film vacuum deposited on a KBr substrate. The four fundamental $F_{1u}$ mode frequencies are indicated, and the large periodic oscillations are due to a Fabry-Perot interference effect in the $C_{60}$ film. The inset shows a fit (dashed line) to the first four interference fringes using a model calculation (see text). (b) Low-frequency portion (450–1700 $cm^{-1}$) of (a). The experimentally determined ir frequencies are tabulated in Table II and are compared with theoretical predictions. (c) Same as in (b) for the high-frequency portion (1700–3000 $cm^{-1}$) of the figure.

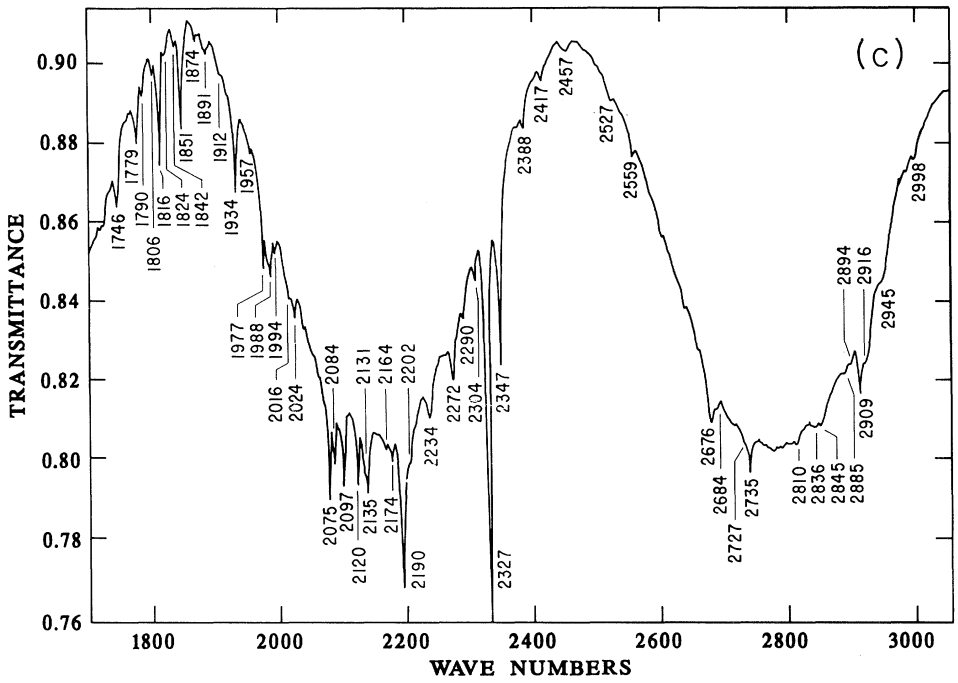


FIG. 1. (*Continued*).

a background exhibiting broad ($\sim$500-cm$^{-1}$ period), large amplitude oscillations. These oscillations are due to an interference between the beams suffering various multiple internal reflections inside the $C_{60}$ film (Fabry-Perot fringes). The inset to Fig. 1(a) shows a fit (dashed line) of the standard functional form for these fringes to data from a film of unknown thickness and refractive index on a KBr substrate ($n=1.5$). Fitting the first four fringes in the spectrum of Fig. 1(a), we have obtained a film thickness $d=4.1$ $\mu$m (close to that determined directly by the film thickness monitor) and a value for the core dielectric constant $\varepsilon_{\text{core}}=3.9$, which is the electronic contribution to the static dielectric function. This latter result is in good agreement with the value $\varepsilon_{\text{core}}=4.0\pm0.05$, also obtained previously from interference fringes in the ir spectrum,[11] and may be compared to $\varepsilon_{\text{core}}=4.4\pm0.2$ deduced by low-frequency capacitance studies.[12] Whereas isolated molecules generally exhibit narrow first- and second-order ir and Raman features, most crystalline solids show only narrow first-order vibrational features ($k=0$ selection rule) and very broad second-order features (due to phonon dispersion). Therefore, the numerous, well-resolved, higher-order ir lines seen in Fig. 1 are taken as further independent evidence for the weak intermolecular interactions in solid $C_{60}$. Thus the vibrational properties of an isolated $C_{60}$ molecule should explain well the intramolecular vibrational modes in solid $C_{60}$.

From group-theoretical arguments, the expected number of *second-order* lines in the ir spectrum of an isolated $C_{60}$ molecule should be very large [ a total of 384 ($\nu_i+\nu_j$) combination modes]. Since ir-active modes have odd parity, no overtone modes are expected in the second-order ir spectrum for $C_{60}$. The total number of combination modes can be found by counting the number of times the symmetry $F_{1u}$ is contained in the direct product $n_i\Gamma_i\otimes n_j\Gamma_j$, where $\Gamma_i$ (or $\Gamma_j$) denotes the symmetry of one of the irreducible representations of the $I_h$ group, and $n_i$ (or $n_j$) is the number of vibrational modes with symmetry $\Gamma_i$ (or $\Gamma_j$). The 46 distinct mode frequencies for a $C_{60}$ molecule which were previously used for the low-temperature analysis of the higher-order Raman spectra[8] are tabulated as Table I. The direct products $\Gamma_i\otimes\Gamma_j$ which characterize the second-order combination modes can be calculated by using the character table for the $I_h$ group.[1,3] For example, the direct product $F_{1g}\otimes F_{1u}=A_u+F_{1u}+H_u$ contains $F_{1u}$ once, which indicates that an ir-active combination mode exists in the second-order ir spectrum arising from the $F_{1u}$ and $F_{1g}$ vibrations. Not all mode combinations yield $F_{1u}$ symmetry in the direct product. For instance, $H_g$ and $F_{1u}$ modes do not result in ir-active combination modes in the second-order spectrum since $G_g\otimes F_{1u}=F_{2u}+G_u+H_u$ does not contain $F_{1u}$.

In principle, the second-order ir spectrum, just like the second-order Raman spectrum,[8] could provide a method for determining the frequencies of optically silent vibrational modes ($A_u$, $F_{1g}$, $F_{2g}$, $F_{2u}$, $G_g$, $G_u$, and $H_u$). The observation of some of the higher-order ir lines in Fig. 1 suggests, on the basis of the group-theoretical arguments given above, that certain modes $\Gamma_i$ which are silent in the first-order ir or Raman processes many participate in the higher-order ir spectrum. By making small adjustments in the frequencies of the silent modes, and using the accepted experimental frequencies for the $A_g$, $H_g$, and $F_{1u}$ modes,[1] we have been able to assign most of the observed lines to second-order combination modes (Table II). The silent mode frequencies (denoted by "*b*" in Table I) have

TABLE I. Experimentally determined mode frequencies for the fundamental vibrations in an isolated $C_{60}$ molecule. First-order ir- and Raman-active modes have $F_{1u}$ and $(A_g, H_g)$ symmetries, respectively. The frequencies of the optically silent modes ($A_u$, $F_{1g}$, $F_{2g}$, $F_{2u}$, $G_g$, $G_u$, and $H_u$) marked with "*b*" have been adjusted to obtain the best overall agreement between the experimental and calculated second-order Raman and ir spectra. The superscript "*i*" denotes ir line frequencies identified with $^{13}C$ isotope-activated modes.

| Even parity | | Odd parity | |
|---|---|---|---|
| $\nu_i(R)$ | Frequency ($cm^{-1}$) | $\nu_i(R)$ | Frequency ($cm^{-1}$) |
| $\nu_1(A_g)$ | 497.5 | $\nu_1(A_u)$ | 1143.0$^i$ |
| $\nu_2(A_g)$ | 1470.0$^i$ | | |
| | | $\nu_1(F_{1u})$ | 526.5 |
| $\nu_1(F_{1g})$ | 502.0$^b$ | $\nu_2(F_{1u})$ | 575.8 |
| $\nu_2(F_{1g})$ | 975.5$^b$ | $\nu_3(F_{1u})$ | 1182.9 |
| $\nu_3(F_{1g})$ | 1357.5$^b$ | $\nu_4(F_{1u})$ | 1429.2 |
| $\nu_1(F_{2g})$ | 566.5$^b$ | $\nu_1(F_{2u})$ | 355.5$^b$ |
| $\nu_2(F_{2g})$ | 865.0 | $\nu_2(F_{2u})$ | 680.0 |
| $\nu_3(F_{2g})$ | 914.0 | $\nu_3(F_{2u})$ | 1026.0$^b$ |
| $\nu_4(F_{2g})$ | 1360.0 | $\nu_4(F_{2u})$ | 1201.0$^b$ |
| | | $\nu_5(F_{2u})$ | 1576.5$^b$ |
| $\nu_1(G_g)$ | 486.0$^b$ | | |
| $\nu_2(G_g)$ | 621.0 | $\nu_1(G_u)$ | 399.5$^b$ |
| $\nu_3(G_g)$ | 806.0 | $\nu_2(G_u)$ | 760.0$^i$ |
| $\nu_4(G_g)$ | 1075.5$^b$ | $\nu_3(G_u)$ | 924.0$^b$ |
| $\nu_5(G_g)$ | 1356.0$^b$ | $\nu_4(G_u)$ | 970.0 |
| $\nu_6(G_g)$ | 1524.5$^{b,i}$ | $\nu_5(G_u)$ | 1310.0 |
| | | $\nu_6(G_u)$ | 1446.0$^b$ |
| $\nu_1(H_g)$ | 273.0 | | |
| $\nu_2(H_g)$ | 432.5 | $\nu_1(H_u)$ | 342.5$^b$ |
| $\nu_3(H_g)$ | 711.0$^i$ | $\nu_2(H_u)$ | 563.0$^b$ |
| $\nu_4(H_g)$ | 775.0$^i$ | $\nu_3(H_u)$ | 696.0$^b$ |
| $\nu_5(H_g)$ | 1101.0$^i$ | $\nu_4(H_u)$ | 801.0 |
| $\nu_6(H_g)$ | 1251.0 | $\nu_5(H_u)$ | 1117.0$^{b,i}$ |
| $\nu_7(H_g)$ | 1426.5 | $\nu_6(H_u)$ | 1385.0 |
| $\nu_8(H_g)$ | 1577.5 | $\nu_7(H_u)$ | 1559.0$^b$ |

been refined here to optimize the overall agreement between the experimental values obtained from both the second-order ir *and* Raman[8] spectra and the anticipated $(\nu_i+\nu_j)$ values. Listed in Table II are the observed and calculated ir mode frequencies obtained from this work and previous studies. In a few cases, more than one predicted combination mode frequency falls within $\pm 5$ $cm^{-1}$ (but most of them are within $\pm 2$ $cm^{-1}$) of the frequency of a particular higher-order ir feature. In such cases, the ir frequency determined experimentally is repeated in the table and assigned to more than one combination mode (see Table II). Overall, the difference between the calculated and observed frequencies is $\pm 4$ $cm^{-1}$, with very few exceptions. Of course, it is possible that some of the observed lines with frequencies $\nu \gg 2H_g(1)$ ($=2\times 272$ $cm^{-1}$) might be associated with third- and higher-order processes. Finally, it should be mentioned that some of the observed lines in Table II may be shifted slightly in frequency due to a Fermi resonance, a phenomenon in which a fundamental mode resonates with a combination mode. This effect is not included in our analysis.

Since the natural abundance of $^{13}C$ is approximately 1.1%, 34.4% of the molecules in our film should be monosubstituted $^{13}C^{12}C_{59}$ molecules (i.e., each of these molecules contains one $^{13}C$ and 59 $^{12}C$ atoms and 11.4% of the molecules should be $^{13}C_2{}^{12}C_{58}$). The lower symmetry ($C_{2h}$) of the monosubstituted $^{13}C^{12}C_{59}$ molecule is expected to activate all ir-silent modes that would otherwise be inactive in isotopically pure $C_{60}$, as previously observed, for example, in the vibrational spectra of benzene.[13] In fact, our ir spectrum exhibits some weak lines whose frequencies are found to be in good agreement with certain fundamental mode frequencies: $H_g(3)$, $G_u(2)$, $H_g(4)$, $H_g(5)$, $H_u(5)$, $A_u(1)$, $A_g(2)$, and $G_g(6)$; these modes are therefore assigned to isotopically activated modes and they are identified by the superscript "*i*" in Tables I and II. However, not all of these fundamental mode frequencies have been uniquely determined. For instance, the lines assigned as $H_g(4)$, $H_u(5)$, and $A_g(2)$ in Table II can also be identified alternatively with the second-order combination modes "$H_g(2)+H_u(1)$," "$F_{2u}(2)+H_g(2)$" [or "$H_g(4)+H_u(1)$"], and "$G_u(2)+H_g(3)$" [or "$H_g(4)+H_u(3)$"], respectively, with comparable accuracy (see Table II). As expected, the frequency shift due to the monosubstitution of $^{13}C$ isotopes is found to be small (less than 2 $cm^{-1}$, in most cases). Isotopic activation of silent $C_{60}$ modes was also reported

TABLE II. Symmetry assignments for experimental ir lines observed in the transmission spectrum of $C_{60}$ films deposited on KBr substrates. The labels "*s*" and "*w*" indicate, respectively, shoulders and weak features in the observed spectrum. As in Table I, the superscript "*i*" denotes $^{13}C$ isotope-activated modes.

| Identification | Model | Expt | Identification | Model | Expt |
|---|---|---|---|---|---|
| $F_{1u}(1)$ | 526.5 | 526.5 | $H_u(1)+G_g(1)$ | 828.5 | 822.9 |
| $F_{1u}(2)$ | 575.8 | 575.8 | $F_{2g}(1)+H_u(1)$ | 909 | 907.8*w* |
| | | 641.7*w* | $F_{2u}(2)+H_g(1)$ | 953 | 956.9*s* |
| $G_u(1)+H_g(1)$ | 672.5 | 673.5 | $F_{1u}(1)+H_g(2)$ | 959 | 956.9*s* |
| $H_g(3)$ | 711.0$^i$ | 712.1 | $H_u(1)+G_g(2)$ | 963.5 | 961.7 |
| | | 738.1 | $F_{2g}(1)+G_u(1)$ | 966 | 961.7 |
| $G_u(2)$ | 760.0$^i$ | 757.4*w* | $G_g(2)+G_u(1)$ | 1020.5 | 1015.7 |
| | | 770.9*s* | $G_u(2)+H_g(1)$ | 1033 | 1036.9 |
| $H_g(4)$ | 775.0$^i$ | 774.7 | $H_g(3)+H_u(1)$ | 1053.5 | 1058.1*w* |
| $H_g(2)+H_u(1)$ | 775 | 774.7 | $H_g(5)$ | 1101.0$^i$ | 1099.6 |
| $F_{1u}(1)+H_g(1)$ | 799 | 808.5*w* | $F_{2u}(2)+H_g(2)$ | 1112.5 | 1114.0 |

TABLE II. (*Continued*).

| Identification | Model | Expt | Identification | Model | Expt |
|---|---|---|---|---|---|
| $H_u(5)$ | 1117.0[i] | 1114.0 | $G_g(4)+H_u(4)$ | 1876.5 | 1874.5 |
| $H_g(4)+H_u(1)$ | 1117.5 | 1114.0 | $F_{2g}(1)+G_u(5)$ | 1876.5 | 1874.5 |
| $A_u(1)$ | 1143.0[i] | 1141.0 | $F_{1g}(1)+H_u(6)$ | 1887 | 1890.9 |
| $F_{2u}(1)+G_g(3)$ | 1161.5 | 1164.1 | $H_g(4)+H_u(5)$ | 1892 | 1890.9 |
| $F_{2u}(2)+G_g(1)$ | 1166 | 1164.1 | $F_{2u}(4)+H_g(3)$ | 1912 | 1912.1*w* |
| $F_{1u}(3)$ | 1182.9 | 1182.9 | $F_{1g}(1)+F_{1u}(4)$ | 1931.2 | 1934.3 |
| $G_u(3)+H_g(1)$ | 1197 | 1196.9 | $F_{1g}(3)+F_{1u}(2)$ | 1933.3 | 1934.3 |
| $F_{1g}(1)+H_u(3)$ | 1198 | 1196.9 | $F_{1u}(3)+H_g(4)$ | 1957.9 | 1957.4*w* |
| $G_g(3)+G_u(1)$ | 1205.5 | 1203.7 | $F_{2u}(4)+H_g(4)$ | 1976 | 1976.7 |
| $F_{2g}(2)+H_u(1)$ | 1207.5 | 1213.3 | $G_u(1)+H_g(8)$ | 1977 | 1976.7 |
| $H_g(2)+H_u(4)$ | 1233.5 | 1234.5 | $H_g(7)+H_u(2)$ | 1989.5 | 1988.3 |
| $F_{1u}(1)+H_g(3)$ | 1237.5 | 1234.5 | $H_g(2)+H_u(7)$ | 1991.5 | 1994.1*w* |
| $G_u(4)+H_g(1)$ | 1243 | 1242.2 | $A_g(2)+F_{1u}(1)$ | 1996.5 | 1994.1*w* |
| $G_g(1)+G_u(2)$ | 1246 | 1242.2 | $F_{2g}(1)+G_u(6)$ | 2012.5 | 2016.2*s* |
| $F_{2g}(3)+H_u(1)$ | 1256.5 | 1258.6 | $G_u(5)+H_g(3)$ | 2021 | 2023.9 |
| $F_{1u}(2)+H_g(3)$ | 1286.8 | 1289.4 | $G_u(3)+H_g(5)$ | 2025 | 2023.9 |
| $G_g(1)+H_u(4)$ | 1287 | 1289.4 | $G_u(4)+H_g(5)$ | 2071 | 2075.0 |
| $F_{1g}(1)+H_u(4)$ | 1303 | 1306.8 | $G_u(5)+H_g(4)$ | 2085 | 2083.7 |
| $F_{2g}(1)+G_u(2)$ | 1326.5 | 1329.9*w* | $H_g(3)+H_u(6)$ | 2096 | 2097.2 |
| $H_g(4)+H_u(2)$ | 1338 | 1342.5 | $F_{2u}(3)+G_g(4)$ | 2101.5 | 2097.2 |
| $G_g(3)+H_u(2)$ | 1369 | 1375.2*w* | $F_{2g}(4)+G_u(2)$ | 2120 | 2120.3 |
| $G_g(2)+G_u(2)$ | 1381 | 1375.2*w* | $F_{2u}(3)+H_g(5)$ | 2127 | 2131.4*s* |
| $F_{1u}(4)$ | 1429.2 | 1429.2 | $F_{1u}(4)+H_g(3)$ | 2140.2 | 2134.8 |
| $H_g(5)+H_u(1)$ | 1443.5 | 1438.9*s* | $F_{2g}(4)+H_u(4)$ | 2161 | 2163.7 |
| $F_{2u}(3)+H_g(2)$ | 1458.5 | 1462.0*s* | $F_{2g}(2)+G_u(5)$ | 2175 | 2174.3 |
| $A_g(2)$ | 1470.0[i] | 1468.7 | $G_u(3)+H_g(6)$ | 2175 | 2174.3 |
| $G_u(2)+H_g(3)$ | 1471 | 1468.7 | $G_u(2)+H_g(7)$ | 2186.5 | 2189.7 |
| $H_g(4)+H_u(3)$ | 1471 | 1468.7 | $G_g(3)+H_u(6)$ | 2191 | 2189.7 |
| $F_{2g}(3)+H_u(2)$ | 1477 | 1479.3*s* | $F_{1u}(4)+H_g(4)$ | 2204.2 | 2202.2*s* |
| $F_{2u}(2)+G_g(3)$ | 1486 | 1483.2 | $H_g(7)+H_u(4)$ | 2227.5 | 2234.1 |
| $F_{2g}(1)+G_u(3)$ | 1490.5 | 1495.7 | $H_g(3)+H_u(7)$ | 2270 | 2271.7 |
| $G_u(1)+H_g(5)$ | 1500.5 | 1495.7 | $H_g(8)+H_u(3)$ | 2273.5 | 2271.7 |
| $G_g(3)+H_u(3)$ | 1502 | 1501.5 | $F_{2u}(5)+H_g(3)$ | 2287.5 | 2290.0 |
| $F_{1g}(2)+F_{1u}(1)$ | 1502 | 1501.5 | $F_{2u}(4)+H_g(5)$ | 2302 | 2303.8 |
| | | 1508.2*w* | $G_g(5)+G_u(4)$ | 2326 | 2326.6 |
| $F_{2u}(3)+G_g(1)$ | 1512 | 1514.0*w* | $G_u(3)+H_g(7)$ | 2350.5 | 2346.8 |
| $H_g(3)+H_u(4)$ | 1512 | 1514.0*w* | $G_g(4)+G_u(5)$ | 2385.5 | 2388.3 |
| $G_g(6)$ | 1524.5[i] | 1523.7*w* | $G_u(5)+H_g(5)$ | 2411 | 2417.2 |
| $G_u(2)+H_g(4)$ | 1535 | 1531.4*s* | $F_{2u}(3)+H_g(7)$ | 2452.5 | 2456.7 |
| $F_{1g}(2)+H_u(2)$ | 1538.5 | 1538.1 | $G_g(4)+H_u(6)$ | 2460.5 | 2456.7 |
| $G_g(2)+G_u(3)$ | 1545 | 1545.8*s* | $F_{1u}(4)+H_g(5)$ | 2530.2 | 2527.1 |
| $G_g(3)+G_u(2)$ | 1566 | 1570.9 | $F_{2u}(4)+G_g(5)$ | 2557 | 2558.9 |
| $H_g(4)+H_u(4)$ | 1576 | 1570.9 | $F_{2u}(5)+H_g(5)$ | 2677.5 | 2675.5 |
| $3F_{1u}(1)$ | 1579.5 | | $F_{1u}(4)+H_g(6)$ | 2680.2 | 2684.2*s* |
| $F_{2u}(1)+H_g(6)$ | 1606.5 | 1607.5 | $F_{2u}(4)+G_g(6)$ | 2725.5 | 2726.6*s* |
| $G_g(3)+H_u(4)$ | 1607 | 1607.5 | $G_u(5)+H_g(7)$ | 2736.5 | 2735.3 |
| $3F_{1u}(2)$ | 1727.4 | | $F_{2u}(4)+H_g(8)$ | 2778.5 | 2772.9*w* |
| $G_u(4)+H_g(4)$ | 1745 | 1746.3 | $H_g(7)+H_u(6)$ | 2811.5 | 2809.5 |
| $F_{1u}(1)+H_g(6)$ | 1777.5 | 1779.1 | $G_g(6)+G_u(5)$ | 2834.5 | 2836.5 |
| $F_{2u}(2)+H_g(5)$ | 1781 | 1779.1 | $F_{1u}(4)+H_g(7)$ | 2855.7 | 2845.2 |
| $F_{2g}(2)+G_u(3)$ | 1789 | 1789.7*w* | $G_u(5)+H_g(8)$ | 2887.5 | 2884.7*w* |
| $F_{2u}(3)+H_g(4)$ | 1801 | 1806.1*w* | $A_g(2)+F_{1u}(4)$ | 2899.2 | 2894.3*w* |
| $H_g(6)+H_u(2)$ | 1814 | 1815.7 | $G_g(6)+H_u(6)$ | 2909.5 | 2908.8 |
| $H_g(2)+H_u(6)$ | 1817.5 | 1815.7 | $F_{1g}(3)+H_u(7)$ | 2916.5 | 2916.5*s* |
| $F_{1u}(2)+H_g(6)$ | 1826.8 | 1824.4*w* | | | 2945.4*w* |
| $F_{2g}(3)+G_u(3)$ | 1838 | 1841.8*w* | $F_{2u}(5)+H_g(7)$ | 3003 | 2997.5 |
| $F_{2u}(5)+H_g(1)$ | 1849.5 | 1851.4 | $3F_{1u}(3)$ | 3548.7 | |
| $G_g(1)+H_u(6)$ | 1871 | 1874.5 | $3F_{1u}(4)$ | 4287.6 | |

recently in the Raman spectrum of solid $C_{60}$ films.[8]

In analogy with observations of the higher-order Raman spectrum, one might expect that the strongest second-order vibrations would involve one of the four $F_{1u}$ modes. Then by group theory, the most intense second-order ir lines should arise from the direct product $4F_{1u} \otimes n_j \Gamma_j$. This assumption implies that strong ir combination modes should occur for $\Gamma_j$ equal to either $A_g$, $F_{1g}$, or $H_g$, which gives rise to a total of 52 combination modes. However, as can be seen in Table II, only nine of these combination modes are observed. Furthermore, as many as 41 combination modes that do not involve the $F_{1u}$ modes are observed with appreciable intensity. It is interesting to note that: (i) of these 41 modes, 16 come from combinations of modes with $F_{2g}$, $G_g$, and $H_u$ symmetries, all of which are otherwise silent in the first-order ir and Raman spectra, and (ii) 25 of these 41 combination modes involve the $H_g$ modes which are Raman active in the first-order spectrum. Thus it appears experimentally that there is no simple rule (such as an $F_{1u}$ mode should be involved in a strong higher-order ir line) to explain the oscillator strength of the individual second-order lines.

It should also be noted that many second-order combination modes predicted by group theory are omitted from Table II when a nearby feature is not observed experimentally. On the other hand, very few of the frequencies observed experimentally could not be associated with either a second-order ir combination mode or an isotopically activated silent mode. The difficulty in making assignments to particular combination modes can be due to any one (or more) of the following reasons: (i) the anharmonicity responsible for activating the respective combination mode may induce a sizable shift in the mode frequency over that predicted by the sum of the fundamental frequencies of the participating modes; (ii) some of the observed frequencies may be due to third- or higher-order processes, i.e., although the second-order features are generally expected to be more intense, this need not be always the case; and (iii) some of the observed frequencies may be associated with difference modes $(\nu_i - \nu_j)$ instead of sum modes $(\nu_i + \nu_j)$.

Finally, it should be mentioned that it is very doubtful that the ir features assigned to the silent intramolecular modes are activated by crystal-field interactions, since at $T = 300$ K the $C_{60}$ molecules are known to be spinning very rapidly about their fcc lattice sites.[14–16]

The authors are grateful to Dr. P. Zhou and Professor G. W. Lehman for helpful discussions. This work was made possible by the financial support from the Center for Applied Energy Research (University of Kentucky) and NSF Grant No. ERR-91-08764. Research at MIT was funded by NSF Grant No. DMR-92-01878.

[1]P. C. Eklund *et al.*, J. Phys. Chem. Solids **53**, 1391 (1992).
[2]D. S. Bethune *et al.*, Chem. Phys. Lett. **179**, 181 (1991).
[3]G. Dresselhaus, M. S. Dresselhaus, and P. C. Eklund, Phys. Rev. B **45**, 6923 (1992).
[4]W. Krätschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, Nature **347**, 354 (1990).
[5]A. Lucas *et al.*, Phys. Rev. B **45**, 13 694 (1992).
[6]M. K. Nissen, S. M. Wilson, and M. L. W. Thewalt, Phys. Rev. Lett. **69**, 2423 (1992).
[7]C. Coulombeau *et al.*, J. Phys. Chem. **96**, 22 (1992).
[8]Z.-H. Dong *et al.*, Phys. Rev. B **48**, 2862 (1993).
[9]P. H. M. van Loosdrecht, P. J. M. van Bentum, M. A. Verheijen, and G. Meijer, Chem. Phys. Lett. **198**, 587 (1992).
[10]B. Chase, N. A. Herron, and E. Holler, J. Phys. Chem. **96**, 4262 (1992).
[11]A. M. Rao *et al.* (unpublished).
[12]A. F. Hebard, R. C. Haddon, R. M. Fleming, and A. R. Kortan, Appl. Phys. Lett. **59**, 2109 (1991).
[13]P. C. Painter and J. L. Koenig, Spectrochim. Acta **33A**, 1003 (1977).
[14]R. Tycko *et al.*, Science **253**, 701 (1991).
[15]P. A. Heiney *et al.*, Phys. Rev. Lett. **66**, 2911 (1991).
[16]W. I. F. David *et al.*, Europhys. Lett. **18**, 219 (1992).