Vibrational study of ^{13}C-enriched C_{60} crystals

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The infrared (IR) spectrum of solid C_{60} exhibits many weak vibrational modes. Symmetry breaking due to ^{13}C isotopes provides a possible route for optically activating IR-silent vibrational modes. Experimental spectra and a semiempirical theory on natural abundance and ^{13}C-enriched single crystals of C_{60} are presented. By comparing the experimental results with the theoretical results, we exclude this isotopic activation mechanism from the explanation for weakly active fundamentals in the spectra.

The availability of high quality C_{60} single crystals has provided an opportunity for the detailed study of weak vibrational features in the infrared (IR) and Raman spectra of this molecular solid. Recent studies identified some of these modes as being weakly activated symmetry-forbidden modes in IR (Refs. 1–3) and Raman[4,5] measurements. Second-order combination modes were also observed in these spectra. These results enabled the authors to use group theoretical arguments to extract candidates for all 46 vibrational modes of C_{60} from the experimental data.[2,4]

Since the icosahedral (I_h) symmetry of the isolated fullerene molecule allows for only four IR-active modes, this symmetry must be broken by some agent. Possible mechanisms for activating such "silent" modes include ^{13}C isotopic impurities, Van der Waals forces from other C_{60} molecules (crystal field effects), anharmonicity, electric field gradients at surface boundaries, impurities, and dislocations. Several previous works[1,2,4,6] have argued that ^{13}C isotope substitution is a likely agent for activating silent modes since for the natural abundance of ^{13}C, about one-half of all C_{60} molecules would have at least one ^{13}C which would break the I_h symmetry and activate all the vibrational modes. In the present study, we experimentally and theoretically explore this idea by studying C_{60} crystals made from natural abundance and ^{13}C-enriched C_{60}.

The natural abundance ^{13}C single crystals were sublimated as described previously[2] from well-cleaned C_{60} powder commercially produced.[7] Typical crystals have dimensions $\sim 1 \times 1 \times 0.5$ mm. The 8% ^{13}C-enriched crystals were sublimated from enriched soot prepared as reported earlier[8] and their chemical and crystallographic qualities were checked by high-resolution ^{13}C solid state nuclear magnetic resonance (NMR).[9] The isotope enrichment was determined by mass spectrometry, showing that the mass distribution follows a Poisson function. A Bomem MB-155 FTIR spectrometer was used to obtain 2 cm^{-1} resolution IR spectra in the 400–5000 cm^{-1} energy range. The infrared spectra presented here were obtained at room temperature with the crystals mounted over a small aperture with a minimal amount of silver paste. The spectra are referenced to spectra obtained through the empty aperture. The IR spectra of such thick crystals has been shown to be independent of atmosphere,[2] so for experimental simplicity the crystals in this study were exposed to air.

The probability that a C_{60} molecule has n ^{13}C atoms is given by the Poisson distribution,[6] p_n, in agreement with the mass spectrometry of the 8%-enriched ^{13}C samples.[8] This function is presented in Fig. 1 for C_{60} molecules made from natural abundance carbon (1.108% ^{13}C) and from 8% ^{13}C-enriched carbon. The natural abundance probability curve shows that about one-third of the molecules will have exactly one ^{13}C atom which will weakly break the icosohedral symmetry of pure $^{12}C_{60}$. From the 8% probability function we learn that only about 1% of C_{60} molecules will be pure $^{12}C_{60}$; most will have 3 – 7 ^{13}C atoms per fullerene.

The IR data are presented in Fig. 2. The uppermost curve is the transmission of a natural abundance C_{60} single crystal, as published previously.[2] The four IR-active F_{1u} vibrational modes are observed to be completely saturated around their known positions of 527, 576, 1182, and 1427 cm^{-1}. All other observed absorptions are due to IR-forbidden fundamental vibrations or second- (or higher-) order modes[2,1,4,3] which have become weakly active in the crystal. One of the weak modes at 710 cm^{-1} was fitted in a previous study;[2] its intensity (proportional to the square of the plasma frequency of the Lorentz oscil-

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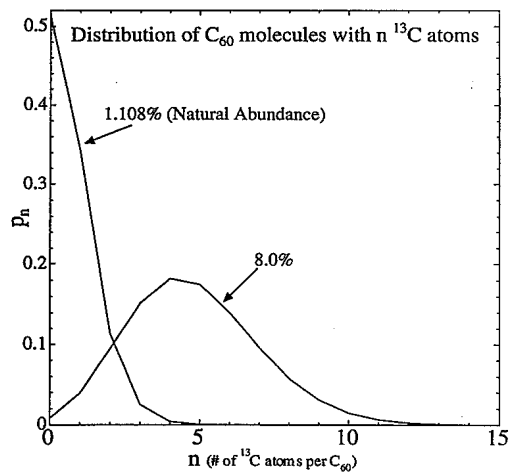

FIG. 1. Plot of the probability function that a C_{60} molecule has n ^{13}C and $(60-n)$ ^{12}C atoms for the natural abundance of ^{13}C and for 8% enriched samples as measured in the present study.

lator, ω_p^2) is approximately 1 order of magnitude smaller than that of a typical F_{1u} mode.

The middle curve of Fig. 2 displays the IR spectrum of an 8% ^{13}C-enriched C_{60} crystal. When comparing this spectrum with that of the natural abundance crystal (top curve of Fig. 2), the primary changes observed are that all of the visible modes have broadened and slightly softened. Note, however, that the relative intensities of the weakly active fundamental and higher-order vibrational modes do not change significantly. Nearly all the features of the 8%-enriched sample transmission spectrum

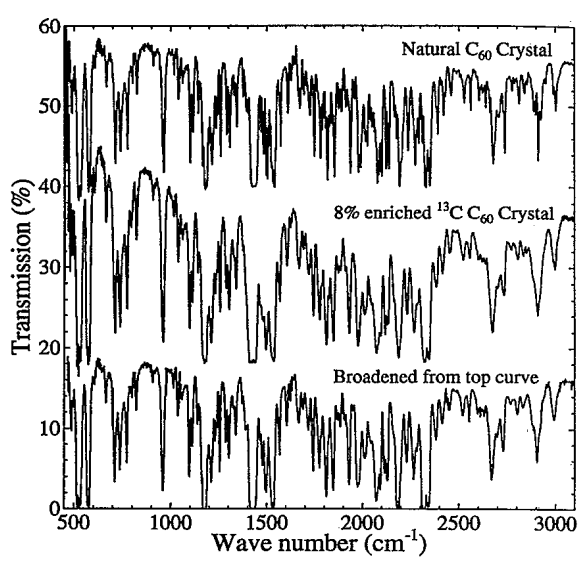

FIG. 2. IR spectra of C_{60} single crystals; the two upper curves have been vertically offset for clarity. The top spectra is from a crystal made from natural abundance ^{13}C C_{60}. The middle curve is the spectra of an 8% ^{13}C-enriched C_{60} crystal. The bottom curve is generated from the top curve using a simple model of frequency shift and the mass distribution given from Fig. 1 for 8% enrichment.

can be modeled by simply broadening the spectrum obtained for the natural abundance crystal using the functions from Fig. 1 and assuming the energy of a mode is proportional to $1/\sqrt{m}$ (like in a simple "ball and spring" model). [This relation between mode broadening and mass distribution was described in greater detail for the $A_g(2)$ Raman fundamental by Guha *et al.*[10]] Carrying this procedure out by applying the 8% Poisson distribution point by point to the top spectra of Fig. 2, we obtain the bottom curve of Fig. 2. A careful comparison of the measured 8%-enriched spectrum and the spectrum generated from the broadening reveals that they are indeed very well matched, indicating that ^{13}C substitutions change the frequency of the mode, but do not influence the intensity. Raman spectra obtained on these samples in which forbidden and higher-order modes are observed give the same results.[11]

If the fundamental modes are being activated by symmetry breaking due to isotopic substitutions, one would expect the ^{13}C-enriched samples to have greater symmetry breaking, and therefore greater IR activity for originally silent modes. To test this, we used a theoretical model of C_{60} based on the bond-charge model of Onida and Benedek[12] [the only change was to use the better experimental values[13] of 1.4 Å for the hexagon-hexagon (6-6) bond length and 1.45 Å for the pentagon-hexagon (5–6) bond length]. The vibrational frequencies calculated with this model are within 3% of the experimental IR and Raman mode frequencies.

The calculation of the IR intensity of a given mode requires, in principle, the knowledge of the electronic eigenstates of the deformed molecule. To avoid the numerical complexity of such an approach we used an approximate procedure, based on the experimentally known IR intensities of the four allowed F_{1u} modes and on the calculated vibrational eigenvectors of the isotopically changed molecule. When expanded in terms of the original eigenvectors of the pure ^{12}C molecule, some or all of the new eigenvectors had components in the directions of the original F_{1u} eigenvectors. Each degenerate species of the unperturbed F_{1u} eigenvectors are chosen to carry their dipole moments in the Cartesian x, y, and z directions. The intensity of each of the four IR-active F_{1u} modes was then taken from experiment[14] and are denoted A_1, A_2, A_3, and A_4. The IR intensity of mode l is then calculated using

$$I_l = \sum_{i=1}^{3} \left(\sum_{j=1}^{4} \sqrt{A_j}\, \tilde{Q}_{jl}^{i} \right)^2 , \qquad (1)$$

where $\tilde{Q}_{jl}^{i}$ is the component of eigenmode l in the direction of the the ith degenerate mode of the original $F_{1u}(j)$ eigenvector; i sums over the triple degeneracies and j sums over the four F_{1u} modes. The isotopic content is modeled by a Monte Carlo simulation: each of the 60 carbon atoms is given a ^{13}C or a ^{12}C mass with appropriate probabilities representing the natural abundance or ^{13}C enrichment (1.108% and 8% ^{13}C, respectively). The dynamical matrix for the resultant molecule was then diagonalized to calculate the eigenvectors, and

Eq. (1) was applied. For a given isotope concentration, this process is repeated until a general sampling of all possible ^{13}C configurations is calculated and the results are averaged together. For the natural abundance case, there are relatively few possible configurations, but for the 8% ^{13}C-enriched case, there are a huge number of configurations. We sampled over 15 000 possible configurations for the 8% case, which should suffice to obtain the correct trends.

We plot the resultant calculated IR intensity for 1.108% and 8% ^{13}C C_{60} molecules in Fig. 3. The Lorentzian widths of all modes have been taken to be uniformly 3 cm^{-1}. The four F_{1u} modes in Fig. 3 have peak heights of approximately 2000 ($\omega_p^2 \sim 5000$ cm^{-1}), so the intensities of the weakly activated modes are approximately a factor of 10^4 smaller. This is in contrast to the experimentally observed intensity ratio of only a factor of $\sim$ 10. Furthermore, the average intensity of the weakly activated modes increases by a factor of 4.45 in the 8% enriched calculation compared to the natural abundance calculation, but no similar increase was seen in the experiment. Very similar theoretical results are given in a recent detailed calculation[15] of the effects of isotopes on the vibrations of C_{60}.

We must therefore conclude that isotopic activation of previously silent modes is not the symmetry-breaking mechanism in C_{60}.

Since the isotope effect is eliminated, the forbidden modes must be activated by another symmetry-breaking mechanism. Surface effects can be ruled out since the phenomenon is independent of sample thickness. Defects in the bulk, like dislocations or vacancies, are also less likely, since the measurements on samples under pressure, or samples subjected to plastic deformation by pressure do not exhibit a dramatic change in these weak lines.[2] Oxygen bound to the fullerenes has been excluded since the number and strength of the weak vibrational modes are unchanged when obtained from C_{60} crystals that have never been exposed to oxygen.[2] Impurities in the crystals are a possibility, however we point out that crystals made from different C_{60} sources and using various growing conditions result in exactly identical IR spectra in every feature.[1–3] A remaining serious candidate is the symmetry breaking due to the first-neighbor interactions between the C_{60} molecules in the solid.

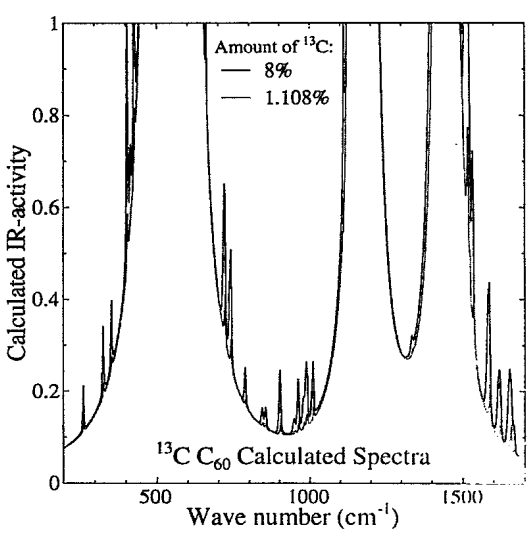

FIG. 3. Calculated IR intensities of vibrational modes in C_{60} with 1.108% and 8% isotopic substitution. The four IR-active F_{1u} modes have intensities of $\sim$ 2000 which are well off scale; the scale is chosen so that the weakly activated symmetry-forbidden modes can be seen.

The first question is, how is it possible that most of the weak fundamentals are visible at room temperature, when the x-ray structure is face centered cubic, with one fullerene molecule per unit cell.[16] In this state the molecules are rotating rapidly and the symmetry-breaking crystal fields fluctuate with this rotation. To clarify this issue, we performed a simple model calculation with a fluctuating external potential breaking the symmetry of an otherwise symmetric arrangement of atoms.[17] All other interactions with the surroundings were represented by a damping constant. We found that a forbidden mode is activated (i.e., the system absorbs energy from the external oscillating electric field in a resonancelike fashion) as long as the correlation time of the fluctuations is not shorter than the lifetime of the resonance (which, in our calculation, was determined by the damping constant).

To apply this idea to the present case, we need to know the natural lifetime of a particular vibrational mode, and the correlation time of the fluctuations of neighbors. The first parameter can be estimated from the linewidth of the well-resolved F_{1u} vibrational modes as measured in detail by Homes *et al.*[18] To avoid complications due to the "inhomogeneous broadening" we take a linewidth from the measurement below the orientational ordering transition temperature ($\gamma = 0.5$ cm^{-1}) and obtain a lifetime of 60 psec. At higher temperatures the lifetime decreases, therefore this is an upper limit. On the other hand the rotational diffusion constant was determined by neutron scattering measurements as $D_R = 1.4 \times 10^{10}$ sec^{-1} at T=260 K, right above the rotational phase transition.[19] This implies that a 60° rotation takes about 130 psec, which is indeed longer than the upper limit to our estimated resonance lifetime.

According the the neutron scattering data, the rotational diffusion constant increases by a factor of 2, to 2.8×10^{10} sec^{-1} at 520 K. However, the lifetime of the resonance is also expected to decrease. In an insulator, the primary channel of phonon decay is due to the interaction between the phonons, and the enhanced population of the phonon states leads to shorter lifetimes at higher temperatures. These considerations lead to an experimentally verifiable prediction: at higher temperatures the "forbidden" lines should either disappear (if the lifetime of the resonance has a weak temperature dependence) or the integrated intensities will not change while the lines broaden (so that the lifetime stays shorter than the fluctuation time). To test this prediction, we measured the IR spectrum of a crystal at elevated temperatures. All observed modes do broaden without a significant change in line intensities up to a temperature of 650 K.

Below $T \sim 250$ K, the orientational ordering transi-

tion temperature, the halting of free rotation of the C_{60} molecules leads to a crystal structure with four fullerenes in the unit cell.[20] In this structure all the *ungerade* modes of the molecule are allowed in the IR by symmetry.[21] The ideal $Pa\bar{3}$ structure retains a center of inversion symmetry at the center of each C_{60} molecule and thus the *gerade* modes are still IR forbidden. However there is a "defect orientation" in the actual structure which will break this inversion symmetry in a significant portion of the C_{60} molecules.[22]

According to these arguments there is reason to believe that the nearest-neighbor surroundings of the molecules provide the symmetry breaking necessary for the activation of the forbidden modes. This mechanism is supported by the fact that many of the weakly active modes exhibit a sharp change when cooled through the orientational ordering phase transition.[3,2] On the other hand the characteristic temperature dependence of the "defect orientation" fraction[22] should lead to a gradual decrease in the intensity of the weakly active IR lines originating from the *gerade* modes (in particular Raman modes), and this was not seen in our experiments.[2]

To summarize, we have shown that isotopic symmetry reduction is *not* the activating mechanism for symmetry-forbidden vibrational modes in C_{60} as has been previously proposed. We have shown that crystal field effects can explain the weak modes both above and below the orientational ordering transition temperature, but further experimental and theoretical work is required to fully understand the nature of the symmetry breaking in fullerene crystals.

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[1] K.-A. Wang, A.M. Rao, P.C. Eklund, M.S. Dresselhaus, and G. Dresselhaus, Phys. Rev. B **48**, 11375 (1993).
[2] Michael C. Martin, Xiaoqun Du, John Kwon, and L. Mihaly, Phys. Rev. B **50**, 173 (1994).
[3] K. Kamarás, L. Akselrod, S. Roth, A. Mittelbach, W. Hönle, and H.G. von Schnering, Chem. Phys. Lett. **214**, 388 (1993); K. Kamarás, K. Matsumoto, M. Wojnowski, and E. Schönherr (unpublished).
[4] Z.-H. Dong, P. Zhou, J.M. Holden, P.C. Eklund, M.S. Dresselhaus, and G. Dresselhaus, Phys. Rev. B **48**, 2862 (1993).
[5] P.H.M. van Loosdrecht, P.J.M. van Bentum, M.A. Verheijen, and G. Meijer, Chem. Phys. Lett. **198**, 587 (1992).
[6] P.C. Eklund, M.S. Dresselhaus, G. Dresselhaus, and Riichiro Saito, Mol. Mat. **4**, 177 (1994).
[7] SES Research Inc., 6008 West 34th Street, Suite H, Houston, TX 77092, USA.
[8] A. Zahab, J.L. Sauvajol, L. Firlej, R. Aznar, and P. Bernier, J. Phys. I (France) **2**, 7 (1992).
[9] R. Kerkoud, P. Auban-Senzier, J. Godard, D. Jerome, J.-M. Lambert, and P. Bernier, C.R. Acad. Sci. Paris **318**, 159 (1994).
[10] S. Guha, J. Menendez, J.B. Page, G.B. Adams, G.S. Spencer, J.P. Lehman, P. Giannozzi, and S. Baroni, Phys. Rev. Lett. **72**, 3359 (1994).
[11] A. Rosenberg and C. Kendziora (unpublished).
[12] G. Onida and G. Benedek, Europhys. Lett. **18**, 403 (1992); **99**, 343 (1992).
[13] K. Hedberg, L. Hedberg, D.S. Bethune, C.A. Brown, H.C. Dorn, R.D. Johnson, and M. de Vries, Science **254**, 410 (1991).
[14] Michael C. Martin, Daniel Koller, and Laszlo Mihaly, Phys. Rev. B **47**, 14 607 (1993); **50**, 6538 (1994).
[15] Y. Tanaka, M. Tokumoto, and Y. Sugawara, Fullerene Sci. Techn. (to be published).
[16] R.M. Flemming, A.P. Ramirez, M.J. Rosseinsky, D.W. Murphy, R.C. Haddon, S.M. Zahurak, and A.V. Makhija, Nature **352**, 787 (1991).
[17] L. Mihaly and Michael C. Martin (unpublished).
[18] C.C. Homes, P.J. Horoyski, M.L.W. Thewalt, and B.P. Clayman, Phys. Rev. B **49**, 7052 (1994); L.R. Narasamihan, D.N. Stoneback, A.F. Hebard, R.C. Haddon, and C.K.N. Patel, *ibid.* **46**, 2591 (1992); V.S. Babu and M.S. Seehra, Chem. Phys. Lett. **68**, 1176 (1992).
[19] R. Tycko, G. Dabbagh, R.M. Fleming, R.C. Haddon, A.V. Makhija, and S.M. Zahurak, Phys. Rev. Lett. **67**, 1886 (1991); D.A. Neuman, J.R.D. Copley, R.L. Cappelletti, W.A. Kamitakahara, R.M. Lindstrom, K.M. Creegan, D.M. Cox, W.J. Romanow, N. Coustel, J.P. McCauley, N.C. Maliszewskyi, J.E. Fischer, and A.B. Smith, *ibid.* **67**, 3808 (1991).
[20] P.A. Heiney, J.E. Fisher, A.R. McFhie, W.J. Romanow, A.M. Denestein, J.P. McCauley, Jr., A.B. Smith III, and D. Cox, Phys. Rev. Lett. **66**, 2911 (1991).
[21] G. Dresselhaus, M.S. Dresselhaus, and P.C. Eklund, Phys. Rev. B **45**, 6923 (1992).
[22] W.I.F. David, R.M. Ibberson, T.J.S. Dennis, J.P. Hare, and K. Prassides, Europhys. Lett. **18**, 225 (1992); W.I.F. David, R.M. Ibberson, J.C. Matthewman, K. Prassides, T.J.S. Dennis, J.P. Hare, H.W. Kroto, R. Taylor, and D.R.H. Walton, Nature **353**, 147 (1991).