Highly Structured Singlet Oxygen Photoluminescence from Crystalline C_{60}

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Crystalline C_{60}, after exposure to air, is shown to exhibit the characteristic luminescence spectrum of singlet molecular oxygen. The role of oxygen is verified by measuring the large isotope shift of the O_2 vibrational mode luminescence replica in a sample prepared with $^{18}O_2$. Detailed spectroscopy reveals novel bands in the spectrum which arise from vibronic coupling of the O_2 transition to the C_{60} molecules. This allows measurement of the C_{60} vibrational spectrum with unparalleled sensitivity and precision from mg-sized samples.

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Since its discovery as a third stable form of carbon [1], C_{60} has quickly emerged as one of the most active topics in physics and chemistry. Much of the current work is focusing on experimental and theoretical studies [2,3] of the 46 distinct vibrational modes of the C_{60} molecule. Selection rules allow only some of these modes to be observed through Raman scattering [4,5] and infrared (IR) absorption spectroscopies [1,6], but lately with the availability of larger samples, neutron inelastic scattering (NIS) techniques have revealed many of the optically inactive modes [7,8]. To date, however, only roughly one-half of the 46 modes have been reported, and limitations in resolution and signal-to-noise ratio, especially above 800 cm^{-1}, have prevented a definitive identification of these.

With much work yet remaining in understanding the intrinsic properties of solid C_{60}, there are understandably very few results that deal with observed properties that are extrinsic to the material. Beyond the deliberate doping with alkali metals to produce superconducting material [9], there is much uncertainty about the role of impurities, particularly oxygen. There have been reports that solid C_{60} is quickly contaminated by O_2 under ambient conditions [10,11] but others suggest that it is impervious to O_2 diffusion [12] except under heavy O_2 exposure and high photon flux [13]. Oxygen contamination could have profound effects on the measured properties of solid C_{60}. In fact, the often mentioned 1468-cm^{-1} Raman mode has recently been attributed to oxygen-contaminated material [10], although this interpretation is not certain.

In this Letter, we report a richly structured photoluminescence (PL) spectrum from air-exposed crystalline C_{60} that is due to the relaxation of O_2 from the singlet excited state $^1\Delta_g$ to the triplet ground state $^3\Sigma_g^-$. This identification is made by comparisons to singlet O_2 luminescence as previously observed in a variety of solvents [14]. The role of O_2 is verified by comparing the energies of the O_2 vibrational mode replica observed in spectra from samples prepared with either $^{18}O_2$ or $^{16}O_2$. Utilizing the high sensitivity of Fourier-transform photoluminescence spectroscopy, we observe many additional replicas of the $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ transition which result from vibronic coupling of this transition to the C_{60} lattice. This is confirmed by the agreement between the mode energies determined from luminescence with those determined from NIS, IR, and Raman spectroscopies. While efficient energy transfer from excited C_{60} to create singlet O_2 has been reported in solutions [15], we believe this to be the first report of singlet oxygen luminescence from a crystalline host material, and coupling to the modes of the host.

The samples were prepared from C_{60} powder (Texas Fullerenes) which had a C_{60} purity (in terms of fullerenes) of 99.9%. Oxygen-free C_{60} single crystals (100–500 μm in size) were grown by sublimation in a temperature gradient under high vacuum in quartz tubes [16], and thick polycrystalline films (grain size $\cong 10$ μm) were obtained in the same process but were deposited nearer the room-temperature region of the quartz tube. Some of the samples were sealed under pure He gas while others were exposed to $^{16}O_2$ and $^{18}O_2$ at 100 °C for 3 h. The spectroscopy was done on a Bomem DA8.01 Fourier-transform interferometer with an InGaAs detector and excitation at 720 nm from a Ti-sapphire laser.

The photoluminescence spectrum from singlet O_2 in organic solvents has attracted considerable attention in itself [14]. The strongest emission is at 7886 cm^{-1} and is due to the $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ transitions. A weaker sideband is also found at 6306 cm^{-1} due to the simultaneous emission of the 1540-cm^{-1} O_2 vibrational mode. This can be compared to the singlet O_2 photoluminescence spectrum from a $^{16}O_2$-exposed C_{60} film, shown in the middle curve of Fig. 1. The dominant feature is a strong doublet at 7782.3 and 7823.8 cm^{-1}. The latter of these is the purely electronic $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ principal transition, and as will be shown, the stronger line at 7782.3 cm^{-1} is a $\cong$41-cm^{-1} replica which likely results from a vibration or libration of the O_2 molecule within the "pocket" it occupies in the C_{60} lattice. As is the case for organic solvents, the transition is again replicated with reduced intensity by the emission of the 1540-cm^{-1} vibrational mode of the O_2 molecule, except that here both the principal line and the $\cong$41-cm^{-1} replica are replicated as indicated by the asterisk in Fig. 1.

Beyond these noted similarities, this spectrum is clearly much more complex than previously observed O_2 spectra,

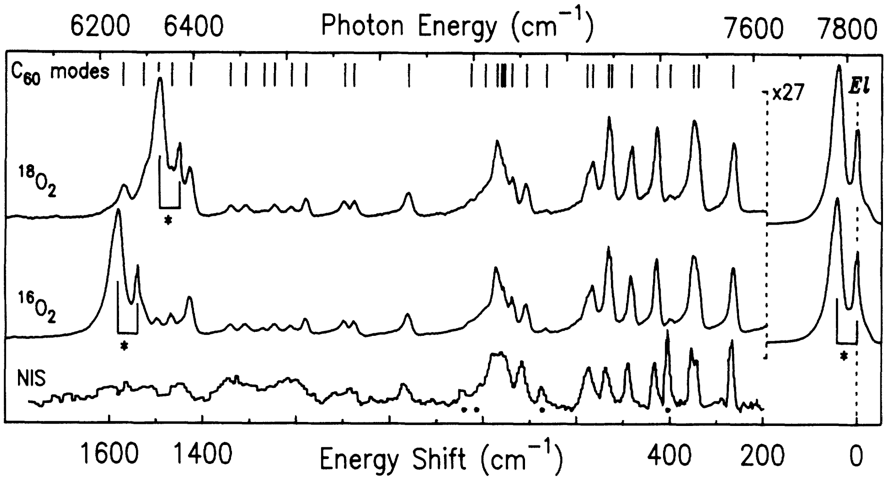

FIG. 1. PL spectra of C_{60} films exposed to $^{18}O_2$, top, and $^{16}O_2$, middle, at $T=4.2$ K, with 720-nm excitation. The photon energy scale for the PL is shown on the top, and on the bottom is a vibrational mode energy scale measured from the purely electronic principal transition, labeled *El*. The asterisks indicate the O_2 vibrational mode replica of the strong doublet. The bottom curve is the NIS data of Ref. [7]. The solid dots mark the *F*-symmetry [7] modes that are only weakly present in the PL.

particularly in the region between the strong doublet and the 1540-cm^{-1} replicas. This rich structure arises from the coupling of the singlet O_2 luminescence transition to many of the expected 46 modes of the C_{60} molecule. The identification of these luminescence features as being due to the emission of C_{60} modes can be confirmed by comparison to NIS data of Coulombeau *et al.* [7] which we have depicted in the bottom curve of Fig. 1.

In the vibrational mode energy region between 200 and 1000 cm^{-1}, the signal-to-noise ratio and resolution of the two spectra are similar, and the structure in the luminescence spectrum is in complete agreement with the NIS data. The only obvious difference is that some modes identified as having *F* symmetry [7] are clearly detected by NIS but are only weakly present in the PL spectrum; these are designated with solid dots along the bottom of Fig. 1. At higher mode energies, our results have a significant advantage over the NIS data and provide important new information on the C_{60} vibrational spectrum. The distinct modes detected in PL are indicated on the top of Fig. 1 with vertical lines and the energies are listed in Table I together with NIS, IR, and Raman data obtained from the literature. In conjunction with these other NIS data, these results allow a very accurate and increasingly complete measurement of modes not already well established through Raman scattering and infrared absorption experiments.

The upper PL spectrum of Fig. 1 was obtained from a vacuum-grown C_{60} film treated in 99.5% $^{18}O_2$. The C_{60}-related replicas are unchanged, but the O_2 vibrational mode replica, again marked by an asterisk, is found at a lower energy shift from the principal line. The ratio of $^{18}O_2$ to $^{16}O_2$ vibrational mode energies, (1452 cm^{-1})/(1540 cm^{-1})$=0.9429$, is almost exactly equal to the inverse ratio of the square roots of the isotopic masses (0.9428). This isotope shift not only conclusively proves the role of O_2, but is also fortuitous in that it allows the observation of two more C_{60} modes which were obscured by the predominant $^{16}O_2$ vibrational replicas.

A similar energy shift between the $^{16}O_2$ and $^{18}O_2$ spectra was also observed in the separation of the two lines comprising the strong doublet. This shift is too small to be seen on the energy scale of Fig. 1, but is more evident in Fig. 2. These spectra were again obtained from an $^{16}O_2$-treated film (dotted curve) and an $^{18}O_2$-treated film (solid curve) at a temperature of 77 K. These higher-temperature spectra also show a thermalizing third line that is higher in energy than the principal line and is clearly the anti-Stokes version of the Stokes replica lying $\cong 41$ cm^{-1} below the principal line. As is clear from the figure, both the Stokes and anti-Stokes shifts are larger for $^{16}O_2$ than for $^{18}O_2$, as expected for a mode that involves motion of the O_2.

It is important to note that although the spectra presented here were obtained from films that were heat treated in O_2, the singlet O_2 PL was also observed in C_{60} films, powders, and crystals exposed to air at ambient temperatures for several days. The detailed structure of the spectra was found to be identical in all of the above-mentioned samples, but the intensity of the luminescence was found to vary. Larger, higher-quality crystals with dimensions approaching 1 mm were found to have the lowest singlet O_2 luminescence intensity. This likely results from slower O_2 diffusion relative to the polycrystalline films. The PL spectrum of the samples that were grown in vacuum and immediately sealed under pure He gas did show a remnant of the O_2-related features but these were extremely weak.

In Fig. 3 we show both the lifetime and integrated intensity of the O_2-related luminescence from C_{60} crystals

TABLE I. Vibrational mode energies in cm^{-1} of C_{60} as measured in this work ($\pm 4\ \text{cm}^{-1}$) as well as by NIS [7], IR absorption [6], and Raman scattering [5].

This work	NIS	IR and Raman
265	264	
	271	270.0 R
339	344	
350	355	
400	404	
428	432	430.5 R
483	488	
		493.0 R
525	526	527 IR
532		
566	563	
578	576	577 IR
665	673	
708	715	708.5 R
739		
755		
761	765	
771		772.5 R
796	813	
827	840	
960	971	
	1044	
1077	1089	
1097	1122	1099.0 R
1180		1183 IR
1211	1217	
1248		1248.0 R
1270		
1309	1327	
1342		
		1426.0 R
1427	1448	1428 IR
1467		1468.5 R
1496		
1524	1520	
1572	1563	1573.0 R
	1603	
	1702	

as a function of the sample temperature. As can be seen in Fig. 3, the lifetime of the luminescence is extremely long at liquid-helium temperatures, over 30 ms. Such long lifetimes have been previously observed for singlet O_2 luminescence in certain solvents which do not couple strongly to the singlet state [17]. As the temperature is increased towards the first-order phase transition of the C_{60} crystal lattice at $T = 260$ K [18,19], the lifetime decreases slowly but still remains long, over 20 ms. Beyond this temperature, however, the lifetime decreases dramatically. This is further evidence that the richly structured singlet O_2 PL does in fact originate from O_2 molecules in the C_{60} lattice. The temperature dependence of the luminescence intensity is also interesting in that it peaks at approximately $T = 80$ K, in the vicinity of the speculated onset of glassy behavior [20,21].

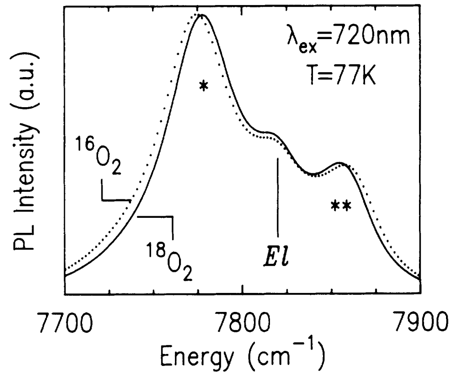

FIG. 2. PL spectra showing the isotope shift of the $\cong 41$-cm^{-1} O_2-related modes in the Stokes (*) and anti-Stokes (**) replicas of the purely electronic (*El*) principal transition.

The spectra presented here were all obtained with excitation energy at 720 nm. 514.5-nm excitation was also effective but typically leads to more background and sometimes extraneous fine structure in the principal line which we suspect to be due to surface damage. The intensity of the PL decreases dramatically for excitation wavelengths longer than $\cong 750$ nm, but still persisted at 900 nm. The onset of intense luminescence at $\cong 750$ nm may be due to the lowest absorption edge of the crystalline C_{60}, perhaps mediated by an exciton. This is just below a relatively strong absorption edge at $\cong 735$ nm that likely corresponds to the band edge.

To conclude, the observation of singlet O_2 luminescence in the bulk of air-exposed C_{60} crystals and films confirms that precautions must be taken to prevent O_2 contamination in studies where pristine material is desired. The luminescence is coupled to the lattice with sufficient strength that the spectrum provides greatly improved information on the modes of molecular C_{60}. It is significant that these spectra can be obtained from milligram-sized samples, allowing for studies of effects

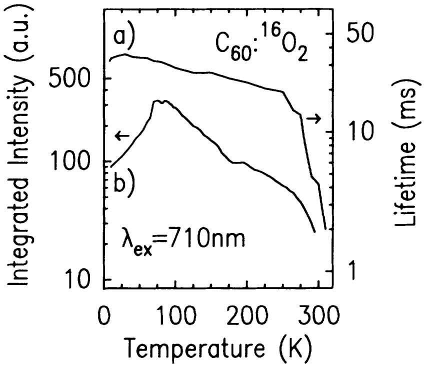

FIG. 3. Lifetime of the O_2-related luminescence, curve *a*, and the integrated intensity of the principal transition and the $\cong 41$-cm^{-1} vibrational mode replicas, curve *b*, as a function of temperature.

such as those of hydrostatic pressure, which are difficult to pursue using the gram-sized samples required for NIS. Also, to the best of our knowledge, this is the first report of highly structured PL from singlet O_2 located in a crystalline lattice and coupling to the modes of that lattice. We are currently attempting to improve the resolution of these measurements to study fine structure in the spectrum that may provide yet more information. We believe this fine structure is related to the mode splittings recently observed by Raman scattering in the low-temperature phase [22].

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Note added.—After submission of our manuscript, we became aware of a recent study by Zhou *et al.* [23] which clarifies the effects of oxygen on the C_{60} Raman spectrum. However, it is not clear whether those effects result from a chemically bonded species of oxygen different from the neutral molecular oxygen which we observe here.

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