RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 52, NUMBER 16 15 OCTOBER 1995-II

Intermolecular charge-transfer excitation in C_{60} films: Evidence from luminescence and photoconductivity

S. Kazaoui, R. Ross,* and N. Minami
National Institute of Materials and Chemical Research, Agency of Industrial Science and Technology, Ministry of International Trade and Industry, 1-1 Higashi, Tsukuba, Ibaraki 305, Japan

(Received 19 June 1995)

C_{60} films have been investigated by means of optical absorption, luminescence, and electric-field-induced luminescence quenching, as well as with steady-state photoconductivity spectroscopies. The drop of the luminescence yield, the increase of the electric-field-induced luminescence-quenching efficiency, and the sharp increase of the photocarrier-generation efficiency above 2.3 eV, are interpreted in terms of branching either in the excitation or relaxation processes involving intermolecular charge-transfer excited states.

I. INTRODUCTION

Fullerenes have attracted much attention owing to their unique molecular and electronic structures. Several properties of the electronic states of C_{60} have already been investigated by a number of spectroscopies including UV-visible absorption, luminescence, and photoconductivity.[1–11] It is of primary importance to elucidate the photophysical properties, with a particular focus on the excitation relaxation processes and the photocarrier generation mechanisms in C_{60} (crystals and films). In the solid state, a specific feature in the range 2.3–3.0 eV has been revealed by UV-visible absorption and luminescence excitation spectra.[9] However, its origins and its implications on the photophysical properties have not been completely understood.

Recently, progress has been made by electroabsorption (EA) measurements on C_{60} films.[12] According to its analysis, charge-transfer (CT) states (intermolecular) have been estimated at 2.7 and 4 eV and Frenkel excitons states (intramolecular) at 1.95 and 2.4 eV.[12,13] Theoretical studies corroborate this view; the spectral intensity in the region 2.5–2.8 eV is enhanced by the effect of intermolecular charge-transfer excitons.[14,15]

Therefore, owing to the fact that these electronic states interact with the electric field, electromodulation of the luminescence is also expected to provide essential information on excitation and relaxation processes. Furthermore, this technique has been increasingly applied to study photogeneration mechanisms. For instance, luminescence quenching and photogeneration in materials such as thionaptheindole, poly(N-vinylcarbazole), and phthalocyanine have already been studied.[16–18]

Herein, we report electric-field-induced luminescence quenching in C_{60} polycrystalline films. The analysis of the excitation energy dependence of luminescence yield, electric-field-induced luminescence quenching, and photocarrier generation efficiencies are expected to elucidate the excitation relaxation and the photocarrier generation mechanisms in solid C_{60}. Optical properties of C_{60} solids will be discussed in terms of Frenkel excitons (intramolecular) and CT states (intermolecular).

II. EXPERIMENT

Films are deposited by sublimation of pure C_{60} powder under vacuum ($p \leq 10^{-6}$ Torr) on sapphire or fused quartz plate (substrate temperature $T_s = 450$ K) predeposited with coplanar interdigitated gold electrodes (gap of 5 μm, total length 10 cm). As observed by scanning electron microscopy and atomic force microscopy, C_{60} films deposited on sapphire are polycrystalline with average grain size of 200 nm.

Owing to the electrode configuration, measurements of UV-visible absorption, photoconductivity, and luminescence, as well as its interaction with an electric field, can be performed on the same samples. Note that these samples have been exposed to air while being loaded into the cryostat. As already reported, oxygen has drastic effects on photoconductivity and luminescence properties.[7,9] However, our previous work clearly shows that oxygen absorbed into the bulk can be mostly deintercalated by annealing at 450 K under 10^{-6} Torr for 12 h. Hereafter, only annealed C_{60} films are considered.

The luminescence emission and excitation measurements have been performed using a spectrofluorometer (JASCO fp-777, cryostat Oxford DN1704) with or without electric field (dc, $E = 10^5$ V cm^{-1}) at 77 K under vacuum. The luminescence emission spectra have been recorded with the conditions $h\nu_{\mathrm{ex}} = 3.75$, 2.75, 2.4, and 2.0 eV with $1.4 \leq h\nu_{\mathrm{em}} \leq 1.8$ eV and the luminescence excitation spectra by monitoring the emission at $h\nu_{\mathrm{em}} = 1.68$, 1.66, and 1.51 eV with $1.77 \leq h\nu_{\mathrm{ex}} \leq 3.75$ eV. It should be pointed out that the luminescence spectra are automatically corrected for the variation of the intensity of the xenon lamp. Using a different experimental setup, the luminescence emission with $h\nu_{\mathrm{ex}} = 2.54$ eV (argon ion laser) has been investigated versus electric field ($E \leq 2.10^5$ V cm^{-1}), light intensity ($N_{\mathrm{ph}} = 6.10^{14}-10^{16}$ s^{-1} cm^{-2}), and temperature ($T = 50-350$ K). UV-visible absorption has been recorded (Shimadzu UV3100S) in the energy range $h\nu = 1.4-6.2$ eV and temperature range T=500–77 K. Photocurrents have been recorded at various excitation energies, electric fields, and temperatures in the ranges $h\nu = 1.5-4.8$ eV (constant photon flux $10^{13}-10^{15}$ s^{-1} cm^{-2}), $E \leq 10^5$ V cm^{-1}, and T=380–77 K, respectively.

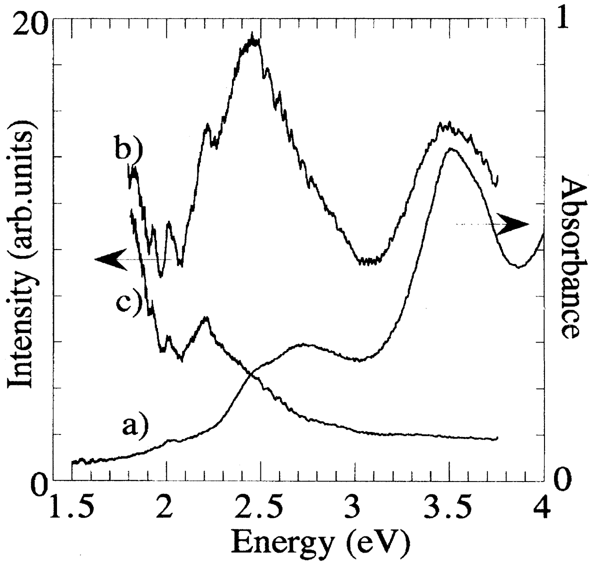

FIG. 1. *a*, UV-visible absorption, *b*, luminescence excitation (monitoring at $h\nu_{em}=1.66$ eV) and *c*, luminescence efficiency spectra ($T=77$ K, annealed C_{60} film, thickness ca. 20 nm).

III. RESULTS AND DISCUSSIONS

The UV-visible absorption spectra of C_{60} thin films are found to retain almost all the characteristic bands observed in solution above 3.0 and below 2.3 eV, although redshifted and broadened (Fig. 1, curve *a*). The most important observation is the appearance of a broad band in the range 2.3–3.0 eV that has no straightforward counterpart in solution. In this broad feature, two peaks have been resolved at 2.51 and 2.85 eV. Their intensities show a discontinuity at 260 K towards low temperature, coinciding with order-disorder phase transition from face-centered cubic to simple cubic, whereas the peak at 3.53 eV (first intramolecular allowed transition) undergoes monotonous increase.[9] This result suggests that the solid-state specific absorption might be related to intermolecular interaction between neighboring C_{60} molecules.

Although several works have been dedicated to C_{60}'s luminescence emission spectra, little has been done on the luminescence excitation spectra over a wide range of energy.[9,19,20] The comparison between the excitation and the absorption spectra of C_{60} films (Fig. 1, curve *b*) shows that the peak at 3.5 eV coincides with the first allowed electronic transition; the broad band in the range 2.3–3.0 eV corresponds to solid-state specific absorption; the fine structures below 2.3 eV belong to intramolecular electronic transitions coupled with vibrational modes.[19] Here also the solid-state specific feature reveals itself in the luminescence excitation spectrum, whereas it does not appear in solution.[20]

Figure 1, curve *c* presents the calculated luminescence efficiency η_l ($h\nu_{em}=1.66$ eV), assuming it is proportional to the luminescence intensity divided by the number of absorbed photons $[1-\exp(-\alpha d)]$ (α absorption coefficient, $d=20$-nm-thick film). Below 2.3 eV, the spectral dependence of η_l reflects that of the luminescence excitation characterized by sharp peaks. An important finding is that above 2.3 eV the efficiency is featureless and clearly decreases with increasing excitation energy. It is also remarkable that the energy-dependent branching observed in C_{60} film above 2.3 eV can be regarded as a solid-state effect because it has no counterpart for isolated molecules in solution.[20]

The drop of the luminescence efficiency above 2.3 eV suggests the existence of branching in the relaxation process from the upper excited states, in competition with internal conversion to the lowest excited states from which the luminescence emission occurs. The origins of the luminescence have been already discussed for excitons and X traps.[1,3,4] The energy-dependent branching might be invoked also in the excitation process from the ground state to upper states. As mentioned earlier, absorption arises in the range 2.3–3.0 eV, peculiar to solid states.

Candidates for the branching either in the excitation or relaxation processes might involve intermolecular charge-transfer excited states. This assumption is relevant to the EA studies[12,13] and to the theoretical calculations[14,15] that predict the existence of a distinct manifold of intramolecular CT states in this energy range.

The solid-state specific feature in the range 2.3–3.0 eV, revealed either by UV-visible absorption or luminescence excitation spectra, involves intermolecular CT states. Their implications can be probed by the electromodulation of the luminescence, because those electronic states can interact with the electric field.

The electric-field-induced luminescence quenching (LQ) has been observed on C_{60} films by recording the luminescence emission spectra. The intensity of the luminescence emission peak (at 1.7 eV with the excitation energy of 3.75 eV) decreases by 12% under electric field ($E=10^5$ V cm^{-1}, $T=77$ K) without appreciable shift or splitting. The integrated luminescence emission in the entire range 1.4–1.8 eV also shows a 10% decrease. On the other hand, no quenching has been observed with 2.0-eV excitation energy, within the experimental resolution. This result demonstrates that the luminescence quenching is excitation energy dependent.

Figure 2 presents the luminescence excitation spectra with and without electric field. The electric-field-induced luminescence-quenching yield has been calculated as follows: $Q_{eff}=1-I(E\neq 0)/I(E=0)$, where $I(E=0)$ and $I(E\neq 0)$ are the intensity without and with electric field, respectively. A striking observation is that the quenching occurs in the range 2.3–3.75 eV, whereas it is absent in the range 1.77–2.3 eV, within the experimental resolution.

It is important to stress that the energy threshold of electric-field-induced luminescence quenching coincides with the drop of luminescence efficiency at 2.3 eV. This occurrence suggests that the energy-dependent branching previously mentioned involves intermolecular CT states which can strongly interact with the electric field. The absence of luminescence quenching in the range 1.77–2.3 eV is consistent with the intramolecular transition (Frenkel-type excitons), whose interaction with the electric field should be weaker. These results are consistent with EA measurements that identified Frenkel exciton states at approximately 1.95 and 2.4 eV and CT states at 2.7 and 4 eV, except for some shift.[12,13]

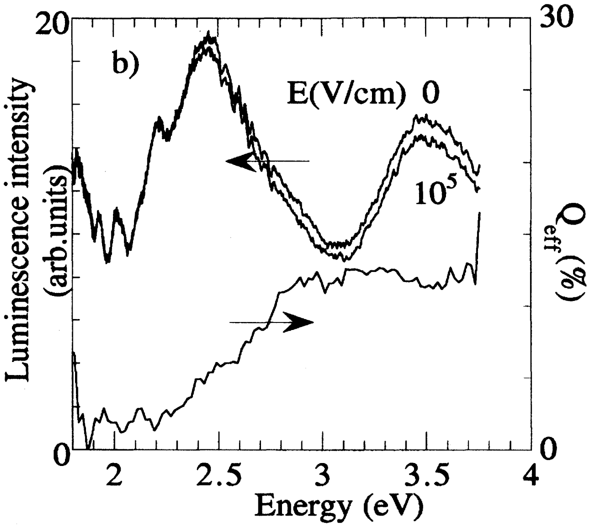

FIG. 2. Luminescence excitation spectra with and without electric field ($E=10^5$ V/cm) (monitoring at $h\nu_{em}=1.66$ eV) and electric-field-induced LQ efficiency spectra ($T=77$ K, annealed C_{60} film, thickness ca. 20 nm).

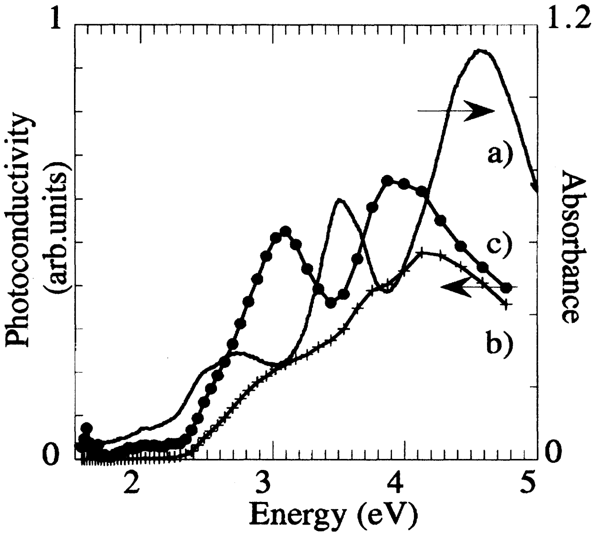

FIG. 3. a, Absorption and b, photoconductivity spectra as well as c, the photocarrier generation efficiencies ($T=77$ K, annealed C_{60} film, thickness ca. 20 nm).

Insight into the electric-field-induced luminescence quenching at $h\nu_{ex}=2.54$ eV has been gained by studying its dependence on several parameters.

(i) Electric-field-induced luminescence quenching has been observed for both thin (thickness ca. 20 nm) and thick films (thickness ca. 200 nm) compared to the light penetration depth (approximately 100 nm at 2.54 eV with absorption coefficient $\approx 10^5$ cm^{-1}). The amplitude of the luminescence quenching is independent of the film's thickness. Inhomogeneous distribution of excitation density might not be a predominant source for electric-field-induced luminescence quenching.

(ii) In the range $E=8.10^4$–2.10^5 V cm^{-1}, Q_{eff} increases as E^3 and $E^{4.5}$ at $T=77$ and 300 K, respectively. The Stark effect on the luminescence behavior can be discarded because the luminescence peaks are not split or shifted and because Q_{eff} does not obey E^2 dependence.

(iii) In the range 0.25–5.0 mW cm^{-2} (photon flux $\approx 6.10^{14}$–10^{16} s^{-1} cm^{-2}), the luminescence intensity increases linearly with excitation intensity either at $T=77$ or 300 K. Q_{eff} is independent of the photon flux at constant electric field and temperature, discarding the effect of nonlinear processes as the origin of the luminescence quenching.

(iv) As a general trend, Q_{eff} increases with the temperature. The quenching yield is weakly temperature dependent below 260 K with a bump at approximately 90 K, whereas it is thermally activated with $E_a=0.025$ eV above 260 K. The features at 90 and 260 K might be related to the well-known phase transitions.

Next, the photocarrier generation process is examined in connection with the electric-field-induced luminescence quenching. Figure 3 presents the steady-state photoconductivity (I_{ph}) measured using coplanar interdigitated Au electrodes with a 5-μm gap. Experimentally, I_{ph} at 77 K depends linearly on photon flux and on electric field in the ranges 10^{13}–10^{15} cm^{-2} s^{-1} and 10–10^4 V cm^{-1}, respectively. The photoconductivity spectrum follows the absorption spectrum in the range 1.5–5.0 eV, indicating that photocarrier generation proceeds via excitation of C_{60} molecules.

The photocarrier generation efficiency is assumed to be proportional to the photoconductivity divided by the number of absorbed photons. Its energy dependence shows weak structures in the range 1.5–2.3 eV, *a sharp increase starting at 2.3 eV*, and several bands above 3 eV. Here also, by a different method, the specific feature in the domain 2.3–3.0 eV has been brought to light.

It is important to stress that the photocarrier generation efficiency is also relevant to the electric-field-induced luminescence quenching, suggesting that carrier generation occurs predominantly through intermolecular CT states above 2.3 eV. Below this energy, photogenerated carriers are due to intramolecular Frenkel excitons. This assumption is corroborated by the activation energy (E_a) of the steady-state photoconductivity that is higher for the excitation energy at $h\nu_1=2.0$ than at $h\nu_2=2.4$ eV (as well as 3.75 eV): for $T>270$ K, $E_a(h\nu_1)=0.3$ and $E_a(h\nu_2)=0.2$ eV; for $T<250$ K, $E_a(h\nu_1)=0.04$ and $E_a(h\nu_2)=0.03$ eV. As expected, while increasing the temperature, the photoconductivity peak at 2.0 eV quickly increases above 270 K and becomes a predominant feature compared to that at 2.3 eV.[21]

Once the luminescence quenching has been attributed to carrier photogeneration by field-assisted dissociation of CT states, it can be speculated that the activation energy of luminescence quenching reflects the binding energy of CT states, approximately 0.025 eV for $T>260$ K.

C_{60}'s photoconductivity has been investigated using different techniques, which all show the threshold for photocarrier generation yield at approximately 2.3 eV, despite some difference in interpretation. Results obtained by the xerographic discharge technique have been analyzed for Onsager surface-mediated dissociation of singlet excitons above 2.3 eV.[6] Transient photoconductivity measurements that reflect photogeneration and recombination processes on C_{60} films suggest two distinct photocarrier generation mechanisms: below 2.3 eV, by exciton-exciton collision ionization, and above, through interband transition.[7]

IV. CONCLUSION

C_{60} films have been investigated by means of optical absorption, luminescence, and electric-field-induced luminescence quenching as well as steady-state photoconductivity spectroscopies.

The solid-state specific feature in the range 2.3–3.0 eV has been assigned to intermolecular CT states. Their implications have been examined. The drop of the luminescence yield concurred both with the increase of the electric-field-induced luminescence-quenching efficiency and with the sharp rise of the photocarrier generation efficiency above 2.3 eV. This observation has been interpreted in terms of branching either in the excitation or relaxation processes involving intermolecular CT states.

A schematic view of the excitation and relaxation processes in solid C_{60} can be drawn. From the ground state, electronic transitions to intramolecular excited states as well as to CT states take place. From the upper excited states, at least two relaxation paths are probable: one to the lowest singlet excited states by internal conversion that ultimately leads to luminescence emission; the other contributes to intermolecular CT state formation. In the range 2.3–3.75 eV, the antibatic behavior has been observed between the luminescence yield and the photocarrier generation efficiency, suggesting that the underlying mechanisms are competing.

In the range 2.3–3.75 eV, carriers are generated by field-assisted dissociation of CT states. In the range 1.7–2.3 eV, photogenerated carriers are due to Frenkel excitons. Their dissociation into free carriers is thermally activated with higher activation energy than for CT states.

Further investigations are in progress to understand the interrelation between photogeneration and luminescence mechanisms in solid C_{60}.

---

[*] On leave from N. V. Kema, Utrechtseweg 310, 6812 AR, The Netherlands.

[1] F. Negri, G. Orlandi, and F. Zerbetto, J. Chem. Phys. **97**, 6496 (1992).

[2] S. Leach *et al.*, Chem. Phys. **160**, 451 (1992).

[3] J. Feldmann *et al.*, Mol. Cryst. Liq. Cryst. **256**, 757 (1994).

[4] D. J. van den Heuvel *et al.*, Chem. Phys. Lett. **231**, 111 (1994).

[5] H. J. Byrne, in Physics and Chemistry of Fullerenes Derivatives, edited by H. Kuzmany, J. Fink, M. Mehring, and S. Roth (World Scientific, Singapore, in press), p. 183.

[6] J. Mort *et al.*, Philos. Mag. Lett. **67**, 77 (1993).

[7] C. H. Lee *et al.*, Phys. Rev. B **48**, 8506 (1993).

[8] G. Giro *et al.*, Chem. Phys. Lett. **211**, 580 (1993).

[9] N. Minami, S. Kazaoui, and R. Ross, Mol. Cryst. Liq. Cryst. **256**, 233 (1994).

[10] S. Kazaoui, R. Ross, and N. Minami, Solid State Commun. **90**, 623 (1994).

[11] R. E. Benner *et al.*, Mol. Cryst. Liq. Cryst. **256**, 241 (1994).

[12] S. Jeglinski *et al.*, Synth. Met. **49-50**, 557 (1992).

[13] P. Petelenz, M. Slawik, and B. Pac, Synth. Met. **64**, 335 (1994).

[14] T. Tsubo and K. Nasu, Solid State Commun. **91**, 907 (1994).

[15] K. Harigaya and S. Abe, Mol. Cryst. Liq. Cryst. **256**, 825 (1994).

[16] J. Noolandi and K. M. Hong, J. Chem. Phys. **70**, 3230 (1979).

[17] Z. D. Popovic, Chem. Phys. **86**, 311 (1984).

[18] J. Kalinowshi, W. Stampor, and P. G. Di Marco, J. Chem. Phys. **96**, 4136 (1992).

[19] H. Schlaich *et al.*, Chem. Phys. Lett. **236**, 135 (1995).

[20] R. M. Williams and J. W. Verhoeven, Spectrochim. Acta **50A**, 251 (1994).

[21] S. Matsuura *et al.*, Phys. Rev. B **51**, 10 217 (1995).