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Raman spectroscopy of C_{60} solid films

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In spite of the simplicity of the Raman spectrum of C_{60}, controversy remains concerning the identification of the Raman spectrum associated with the pure C_{60} solid. In particular, the exact frequency of the pentagonal pinch mode is still an open question. In this paper, the change of the room-temperature Raman spectrum of an oxygen-free C_{60} film as a function of the laser power is reported. As previously reported, two distinct Raman spectra are found: a 1469-cm^{-1} Raman spectrum under a low incident laser power ($P_\lambda = 1$ mW) and a 1459-cm^{-1} Raman spectrum under a moderate incident laser power ($P_\lambda = 50$ mW). The temperature dependences of these two Raman spectra in a large temperature range 10–430 K, and under low, moderate, and high incident laser power are analyzed. The most consistent explanation of these dependences is a phototransformation of oxygen-free C_{60} under the laser irradiation featured by a dominant 1459-cm^{-1} Raman spectrum at room temperature, the 1469-cm^{-1} Raman spectrum being assigned to the pure oxygen-free C_{60}. Our point of view is confirmed by the observation, after a peculiar thermal treatment, of a stable-in-air C_{60} form featured by a 1459-cm^{-1} room-temperature Raman spectrum. Obviously, this result argues against the interpretation of the 1459-cm^{-1} spectrum as that of a pure oxygen-free C_{60} solid.

I. INTRODUCTION

C_{60} continues to attract considerable attention due to the elegant molecular structure and the intriguing structural, dynamic, and electronic properties of the solid phases of the fullerenes. Raman spectroscopy has proved to be a very useful tool to characterize fullerenes and to watch the doping process. Consequently, many papers have been devoted to Raman studies of fullerenes. In spite of the simplicity of the Raman spectrum, controversy remains concerning the exact frequencies of some vibrational modes of the molecule, in particular the pentagonal pinch mode (the most intense Raman line).

Bethune *et al.* have reported the Raman spectrum of a C_{60} film in air; it is dominated by a strongly polarized line at 1469 cm^{-1}.[1] The same observation was also reported by other groups.[2]

Conversely, some authors[3,4] have claimed that the room-temperature Raman spectrum of oxygen-free C_{60} in the range of the tangential modes is dominated by a peak at 1459 cm^{-1}, the 1469-cm^{-1} peak being recovered only upon exposure of the film to oxygen. It must be underlined that their spectra have been taken using a high strength of the laser flux (500 mW/mm^2) and the fact that the 1459-cm^{-1} line was found to be broad and to have a depolarization ratio of about 0.3, as opposed to the expected value of zero, casted some doubts on the interpretation of this line as the totally symmetric Raman mode of C_{60}.

Zhou *et al.*[5] understood these opposite results as a consequence of a phototransformation of oxygen-free C_{60} under a high laser irradiation. In this first scenario, they proposed that the 1459-cm^{-1} line was the Raman signature of a phototransformed phase and that the oxygen presence avoids the C_{60} phototransformation. At $T = 300$ K, a fluence of about 50 mW/mm^2 was sufficient to phototransform solid C_{60} on the time scale of 1 h. They identified the intrinsic pentagonal pinch mode of C_{60} with the line at 1469 cm^{-1} initially observed by Bethune *et al.*[1] Recently, Rao *et al.*[6] discovered that the C_{60} polymerizes under high light excitation and, consequently, they suggested the interpretation of 1459-cm^{-1} line as the signature of a photoinduced polymerization of C_{60}. A recent Raman study of photoexcited C_{60} by Sinha *et al.*[7] is also consistent with this interpretation.

Contrary to this explanation, Hamanaka *et al.*[8] recently observed an intense peak around 1460 cm^{-1} in their room-temperature Raman spectrum measured on a C_{60} single crystal under a low incident laser power ($P_\lambda < 50$ mW/mm^2). They assigned this peak to the intrinsic pinch mode of an oxygen-free C_{60} single crystal. In agreement with this observation, Akers and collaborators explained the coexistence of two Raman spectra, featured by main peaks at 1469 and 1459 cm^{-1}, respectively, by a second scenario. They suggested the coexistence of two distinct phases of C_{60} over a wide temperature range. The 1459-cm^{-1} line is then assigned to the intrinsic pinch mode of oxygen-free C_{60} at room temperature, the 1469-cm^{-1} line corresponding to the same mode in the low-temperature phase.[9,10] This could be observed at room temperature because of the presence of O_2, which would produce, limiting the free rotational motions, the same effect as the order-disorder transition in an oxygen-free C_{60}. A high laser flux would induce a diffusion of the absorbed oxygen out of the solid leading to pure oxygen-free C_{60}.

Finally, van Loosdrecht, van Bentum, and Meijer, reported low-temperature ($T = 40$ K) Raman spectra of C_{60} as a function of the laser irradiation. They observed that under a laser flux of 3000 mW/mm^2, the 1459-cm^{-1} line

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totally replaced the initial 1469-cm^{-1} line; they assigned the 1459-cm^{-1} line to the pentagonal pinch mode in an electronically excited state (long-lived triplet state) of oxygen-free C_{60}, populated upon exposure to high laser flux.[11]

With the objective to give additional information about the debated question of the intrinsic Raman spectrum of solid C_{60} and about the temperature dependence of this spectrum, we have done Raman and photoluminescence investigations of oxygen-free C_{60} films under low, moderate, and high strength of the laser flux in a large temperature range (10–420 K).

This paper is organized as follows. In Sec. III A 1 we discuss the changes of the room-temperature Raman spectrum as a function of laser power and exposure time and show that these changes are sample dependent. We state that the 1469- and the 1459-cm^{-1} Raman spectrum are related to two peculiar forms of solid C_{60}. In Sec. III A 2 we describe the temperature dependence of the Raman spectrum of a defined room-temperature state of an oxygen-free C_{60} film. The most striking result is that, in some films that show a room-temperature Raman spectrum characterized by a dominant 1459-cm^{-1} line, the 1469-cm^{-1} line is restored at low temperature. However, the temperature dependence of this 1469-cm^{-1} peak differs significantly from that measured when it dominates at room temperature. In Sec. III A 3 we discuss the temperature dependence of the Raman spectrum in the high-temperature range (300–430 K). In films, characterized by the 1459-cm^{-1} Raman spectrum at room temperature, we show a remarkable spectral change around 420 K, featured by the emergence of a 1466-cm^{-1} line. All result of Sec. III A, previously performed on different samples and separately interpreted following opposite scenarios, are obtained here on a single sample, which rules out any influence of the sample dependence on their observations.

In Sec. III B we discuss the most important result we have obtained: for an oxygen-free C_{60} film irradiated with a moderate laser power, the slow decrease of the temperature from 430 K to room temperature (RT) leads to a *C_{60} form stable in air at room temperature* characterized by a Raman peak at 1459 cm^{-1}. Clearly, this result seems to definitively argue against the interpretation of the 1459-cm^{-1} spectrum as that of a pure oxygen-free C_{60} form.

From all these results, we conclude that oxygen-free C_{60} film is a very high photosensitive compound and a moderate power laser irradiation leads to a phototransformed state called C_{60}^{PT} associated with the 1459-cm^{-1} Raman spectrum. This state can be stabilized in air following a peculiar thermal treatment. Consequently, we confirm the assignment of the 1469-cm^{-1} Raman spectrum to the one of pure C_{60} form.

II. EXPERIMENTAL

C_{60} films have been grown from material produced by graphite sublimation in arc followed by a liquid chromatography purification and powder annealing at 220 °C in vacuum (10^{-5} mbar) to remove residual solvent.[12] Thin films have been deposited by thermal evaporation of C_{60} powder at 420 °C in vacuum (5×10^{-6} mbar). After deposition, the films were stored and put in a cryostat or furnace under an Ar atmosphere in a glove box.

The spectra were measured in a backscattering arrangement using a standard Coderg T800 triple monochromator spectrometer, an argon-ion laser with the 5145-Å line as the exciting light source, and a C31034 RCA photomultiplier and photon counting electronics. The instrumental linewidth was fixed to be 5 cm^{-1}.

In all the experiments, with the size of the laser spot kept fixed, we analyze the variation of the spectrum directly as a function of the laser power P_λ, which varied in the range 1–200 mW. Note that in these conditions, a power of 10 mW gave a power density of about 50 mW/mm^2.

Spectra were carried out under high vacuum in the temperature range 10–420 K using a conduction cryostate (10–300 K) and a furnace (300–430 K) with the films stuck on a cooper sample holder.

Raman and photoluminescence (PL) spectra were carried out at the same time and with the same experimental conditions. In particular, the volume exposed to the laser beam was identical in the two experiments. This last condition rules out all the discussions about a possible inhomogeneity of the samples in the comparison of the Raman and photoluminescence spectra and consequently allows us to correlate unambiguously the Raman and photoluminescence data.

III. RESULTS

A. Raman spectroscopy of oxygen-free C_{60} solid films

1. The room-temperature Raman spectrum as a function of irradiation

In Figs. 1(a)–1(d) parts (1400–1500 cm^{-1}) of successive Raman spectra measured at the same location of the laser beam on an oxygen-free C_{60} film in high vacuum (dynamical pumping), at room temperature, and under different incident laser powers are displayed. The low-power Raman spectrum [$P_\lambda = 1$ mW, Fig. 1(a)] is dominated by a peak at 1469 cm^{-1}. For an incident power of 50 mW this peak gradually vanishes and a broad feature emerges at 1459 cm^{-1} with increasing the exposure time [Figs. 1(b) and 1(c)]. After the observation of a dominant 1459-cm^{-1} Raman spectrum [an exposure time of about 1 h was necessary, Fig. 1(d)], another Raman spectrum has been taken at the same location of the beam under a low incident laser power ($P_\lambda = 1$ mW) and after that the laser irradiation was blocked for 14 h. The 1459-cm^{-1} line still dominates the spectrum, which states the stability of the C_{60} form associated with the Raman peak at 1459 cm^{-1}. As reported previously, these results can be understood by a photoinduced photopolymerization or by assuming an expulsion of adsorbed oxygen under high laser irradiation leading to a pure oxygen-free C_{60} solid. However, the depolarization ratio ($\rho = I_{VH}/I_{VV}$) of the 1459-cm^{-1} Raman line is about 30%, significantly higher than the depolarization ratio of the 1469-cm^{-1} peak of about 10% (a value of zero is expected for the totally symmetric Raman mode of C_{60}). These data suggest that the 1459-cm^{-1} line is not the intrinsic pinch mode of C_{60} and, consequently, argue in favor of the phototransformation process. On the other hand, similar behaviors have been obtained on different samples and the only significant difference between the results is the sample dependence of the laser flux strength, which is necessary to induce the appearance of the 1459-cm^{-1} line. For the same exposure time, in several films a power of about 1 mW was sufficient, whereas a power of 50 mW was necessary in others films. Thus the laser power that induces a change from the 1469-cm^{-1} Raman spectrum to the 1459-cm^{-1} Raman spectrum is not an intrinsic feature of C_{60}. In addition, it is interesting to note that the use of a high laser power ($P_\lambda = 100$ mW) leads to the appearance of a mode at 1466 cm^{-1} that totally replaces the 1459-cm^{-1} Raman line. The study of the temperature dependence of the Raman spectrum in the high-temperature range (300–430 K) (see Sec. III A 3) allows us to understand this striking result as due to a local heating of the film by the laser beam.

In Figs. 2(a) and 2(b) we compare the room-temperature photoluminescences associated with the 1469-cm^{-1} Raman spectrum and the 1459-cm^{-1} Raman spectrum, respectively. Although the emission spectrum arises in the same region, the shapes of the photoluminescences are significantly different, which suggests changes in the electronic structure of C_{60} under low and moderate laser irradiation.

These room-temperature results give an illustration of the controversy concerning the Raman spectrum of solid C_{60} and the form of solid C_{60} that is associated with each spectrum. Indeed most of them can be understood (i) by considering a process of phototransformation of C_{60} under laser irradiation[2,5–7] or, alternatively, (ii) by assuming that absorbed oxygen diffuses out of the solid upon laser irradiation and dynamical pumping leading to a pure oxygen-free C_{60} solid.[3,9,10] In these two explanations, the room-temperature Raman spectrum of the final state of C_{60} (phototransformed C_{60} and pure oxygen-free C_{60}, respectively) is featured by a peak at 1459 cm^{-1}. However, all spectra reported in this section have been obtained on oxygen-free C_{60} samples; consequently, they provide strong evidence that the phase associated with 1459-cm^{-1} mode is induced by the strong laser light and that the 1469-cm^{-1} mode is associated with pristine, oxygen-free C_{60}. In order to differentiate more clearly these two types of states, the temperature dependence of the Raman spectrum of oxygen-free C_{60} films as a function of laser power has been analyzed.

2. *Temperature dependence of the Raman spectrum in the low-temperature range*

In one experiment the Raman spectrum of an initially nonirradiated oxygen-free C_{60} film is measured at 100 K

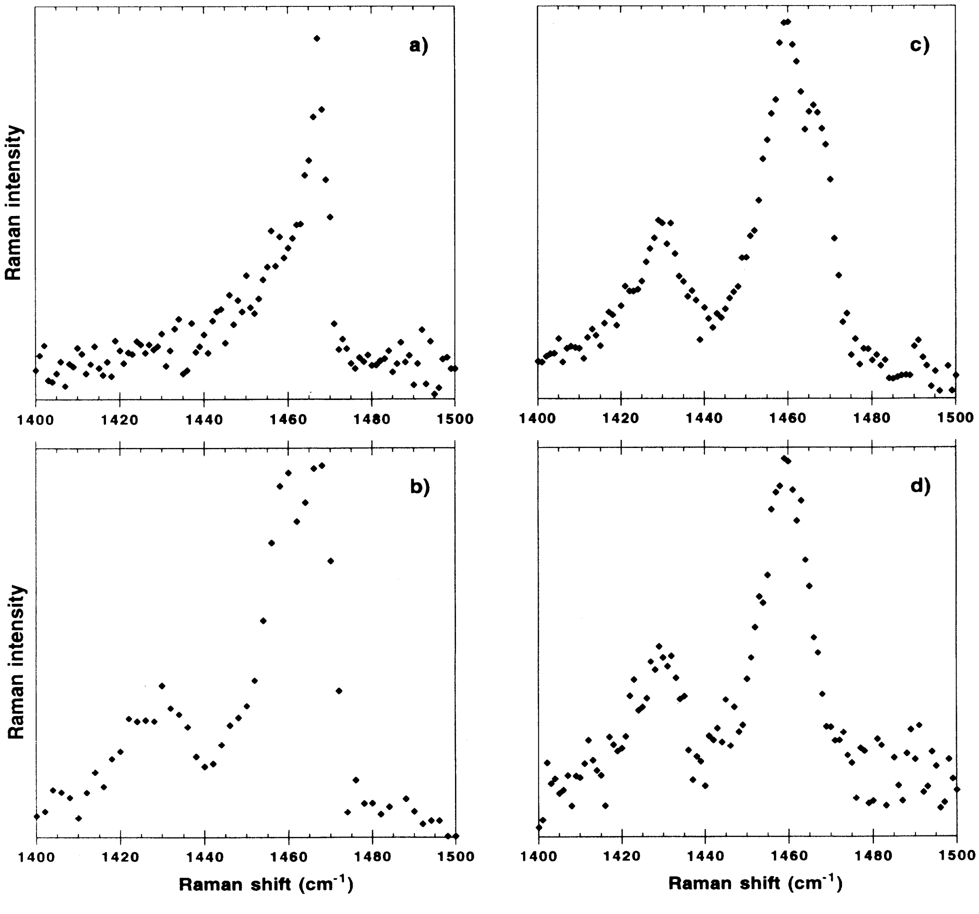

FIG. 1. Room-temperature Raman spectrum of an oxygen-free C_{60} film. (a) $P_\lambda = 1$ mW. (b) $P_\lambda = 50$ mW, after 20 min of exposure to laser radiation. (c) $P_\lambda = 50$ mW, after 40 min of exposure to laser radiation. (d) $P_\lambda = 50$ mW, after 60 min of exposure to laser radiation.

as a function of the incident laser power. We observe that for incident powers $P_\lambda > 10$ mW, which at room temperature induce for the same sample the change of the Raman spectrum from the 1469-cm^{-1} spectrum to the 1459-cm^{-1} spectrum, the low-temperature Raman spectrum is unchanged and the 1469-cm^{-1} line is dominant [Fig. 3(a)]. Using a moderate incident power $P_\lambda = 50$ mW, we follow the temperature dependence of the Raman spectrum from 100 to 300 K [Figs. 3(a)–3(f)]. Clearly, a shoulder at 1459 cm^{-1} appears around the temperature of the phase transition at about 250 K and the 1459-cm^{-1} line is dominant at higher temperature. Our results, which are in agreement with previous data,[10,13] can again be understood by following two scenarios previously proposed. (i) Zhou *et al.* claim that the photochemical "2+2 cycloaddition" reaction that drives the phototransformation of C_{60} requires topological conditions (parallel alignment between reactive double bonds on adjacent molecules), which are only achieved in the plastic phase of C_{60}.[13] In this framework our results confirm the assignment of the 1459-cm^{-1} Raman spectrum as the signature of the phototransformed state of C_{60}. (ii) Alternatively, Akers *et al.*[9,10] explain the same observations by assigning the 1469-cm^{-1} spectrum to the one of the pure C_{60} low-temperature phase and the 1459-cm^{-1} spectrum to one of the pure C_{60} high-temperature phase. In this framework and as expected, the change of the Raman spectrum occurs at the phase transition temperature, around 250 K. However, a shift of an intramolecular mode of about 10 cm^{-1} at the order-disorder phase transition is unusual in a van der Waals molecular crystal.

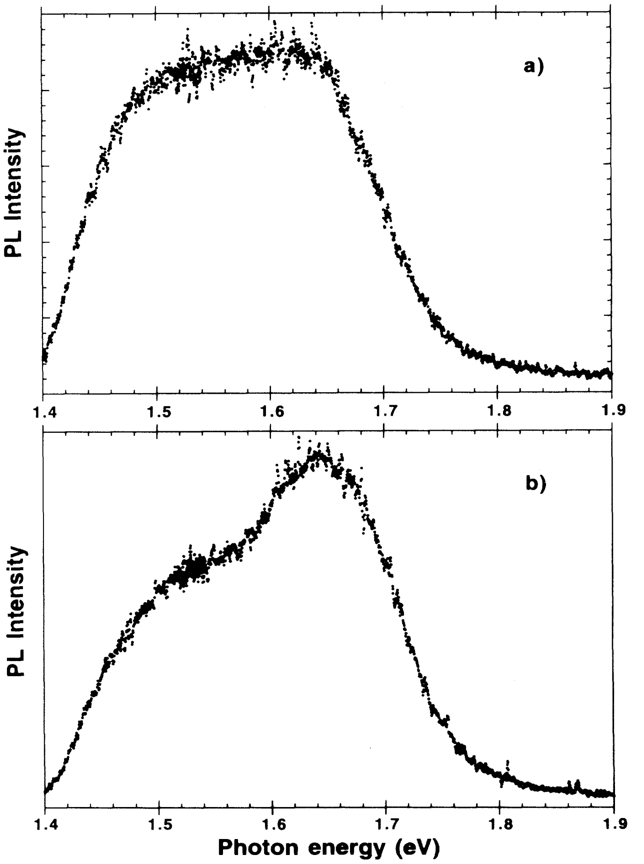

FIG. 2. Room-temperature photoluminescence of an oxygen-free C_{60} film (a) related to the 1469-cm^{-1} Raman spectrum and (b) related to the 1459-cm^{-1} Raman spectrum.

In another experiment we compare the temperature dependence of the Raman spectrum performed on two different locations of the laser beam on the same oxygen-free C_{60} film upon low ($P_\lambda = 2$ mW) and moderate ($P_\lambda = 50$ mW) irradiation. In these experiments, the cooling-heating cycles (RT–10 K–RT) have been monotonically made by steps of 50 K. It took approximately 24 h to complete the cycle.

In Fig. 4(a) the intensity of the 1469-cm^{-1} Raman line is plotted as a function of temperature in an experiment upon low irradiation. Above 250 K the temperature dependence is quite weak; at lower temperature this intensity increases up to a maximum around 90 K and saturates below 90 K. This increase of the 1469-cm^{-1} intensity is anomalous and can be explained as being due to changes in the resonance conditions with the temperature.[14]

Figure 5 shows the dependence of the Raman spectrum measured at another location of the laser beam on the same C_{60} film upon a moderate irradiation ($P_\lambda = 50$ mW). The 1459-cm^{-1} Raman line dominates the room-temperature spectrum and an enhancement of the 1469-cm^{-1} intensity is observed below 120 K, in agreement with previous results.[9,10] The temperature dependence of the 1469-cm^{-1} intensity, displayed in Fig. 4(a), is clearly different from the one measured in the experiment upon low irradiation. In addition, over the entire temperature range, the intensity of the 1459-cm^{-1} line is weakly temperature dependent as shown in Fig. 4(b), which demonstrates that the 1459-cm^{-1} line is not replaced by the 1469-cm^{-1} line at low temperature as previously claimed.[9,10] In this experiment, a weak component is also observed around 1452 cm^{-1}, whose intensity is also weakly temperature dependent [Fig. 4(c)], and no clear hysteristic behavior of the intensity of these Raman lines is displayed in the heating-cooling cycles.

Several other cooling-heating cycles have been done on the same film at other locations of the laser beam, with different laser powers and exposure times. In Fig. 6 the initial ($T = 300$ K) and final ($T = 10$ K) spectra measured in three cycles that essentially differ with regard to the incident power used are shown. In particular, from Raman experiments performed using the lowest incident power of this run [$P_\lambda = 1$ mW, Figs. 6(a) and 6(b)], we state that the 1469-cm^{-1} line dominates the spectrum over the entire temperature range. In the two other cycles, featured by a 1459-cm^{-1} Raman spectrum at room temperature, two opposite behaviors are displayed: (i) in experiments performed under a laser power $P_\lambda = 100$ mW, the 1469-cm^{-1} line drastically increased and became the more intense line at low temperature [Figs. 6(c) and 6(d)]; (ii) con-

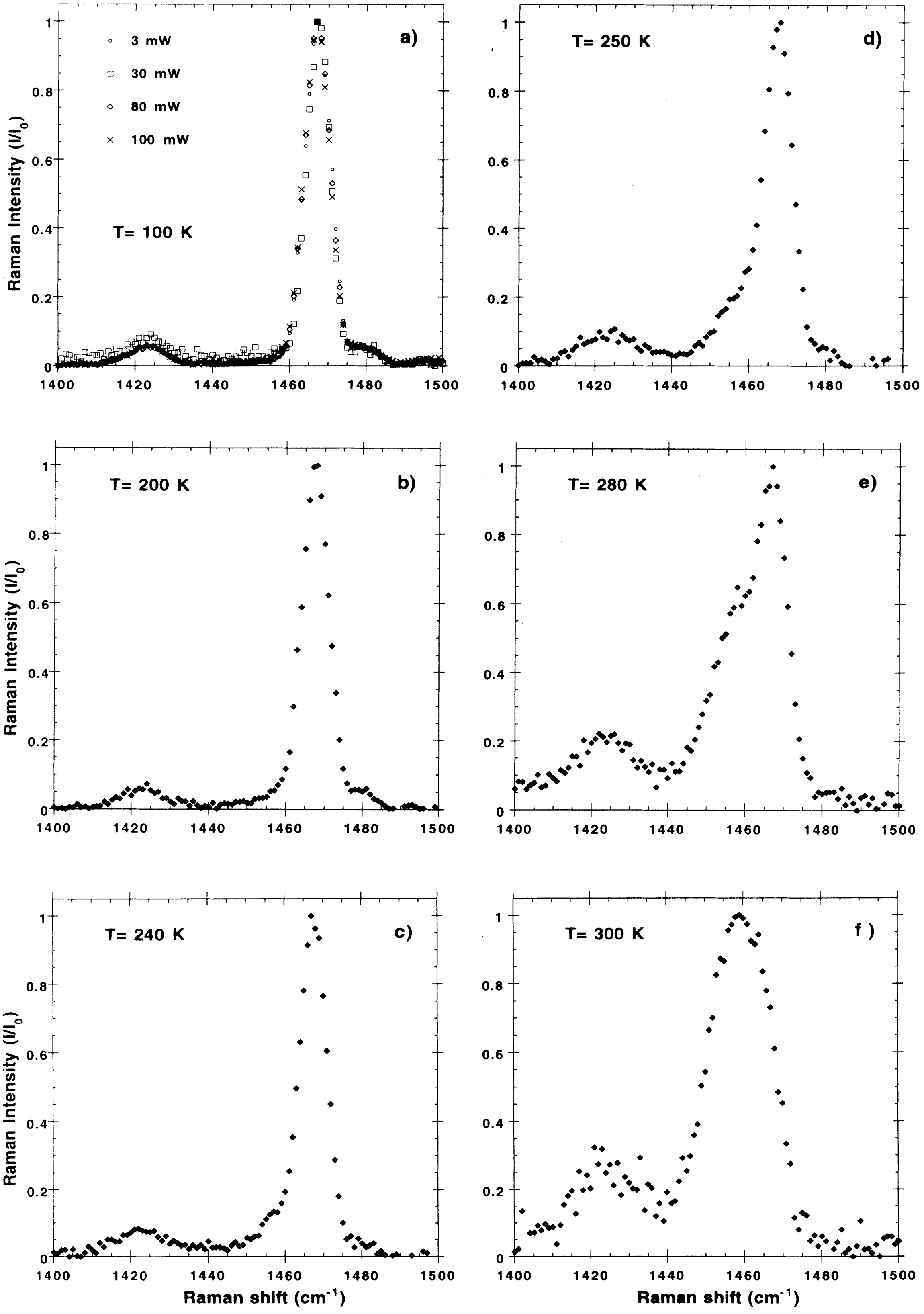

FIG. 3. Raman spectra of an oxygen-free C_{60} film at different temperatures. The film is initially at 100 K and not exposed to a high laser flux. (a) P_λ in the range 3–100 mW and (b)–(f) $P_\lambda = 50$ mW.

versely, in a third cycle, any enhancement of the 1469-cm^{-1} intensity occurred and the 1459-cm^{-1} line always dominated over the entire temperature range [Figs. 6(e) and 6(f)]. In this last experiment a power P_λ of 10 mW was used and the irradiation time was larger than in the previous experiments.

All these dependences can be also explained following the two opposite scenarios previously discussed. In the framework of a phototransformation of oxygen-free C_{60} solid under laser irradiation,[2,5–7] our results can be understood in the following terms: The increase of the 1469-cm^{-1} intensity in the phototransformed C_{60} state is not due to a presence of a large nonphototransformed C_{60} part in the scattering volume. Indeed, in this last assumption the two curves plotted in Fig. 4(a) would display the same dependence. Consequently, we propose that the dependence of the 1469-cm^{-1} intensity is explained by considering that the room-temperature initial state is a solid solution between a phototransformed C_{60} state (called C_{60}^{PT}) and C_{60} molecules, which play the role of impurities. This state can be denoted $(C_{60}^{\mathrm{PT}})_{1-x}(C_{60})_x$, where x is a dilution parameter. In an incomplete phototransformed state [$x \neq 0$, Fig. 6(c)], C_{60} molecules are embedded in the matrix of phototransformed C_{60} and the 1469-cm^{-1} line, which is the intrinsic pinch mode of these C_{60} molecules, emerges at low temperature [Fig. 6(d)]. The increase of the intensity at low temperature is not completely clear at this time, but could be due to changes in the resonance conditions of C_{60} molecules. For a complete phototransformed initial state [$x = 0$, Fig. 6(e)], the 1469-cm^{-1} line does not emerge in the low-temperature Raman spectrum [Fig. 6(f)]. This explanation of our results is alternative to the one derived from the other scenario, which assumes that the 1469-cm^{-1} spectrum is carried by the thermodynamically stable phase at low temperature of pure oxygen-free C_{60} film and that the transition between the high-temperature phase, featured by the 1459-cm^{-1} spectrum, and the low-temperature phase can be attained quickly at high laser irradiation.[9,10] Nevertheless, this latter explanation necessary assumes that the high-temperature phase has a large temperature range of metastability, of about 150 K, which is unusual in molecular crystals.

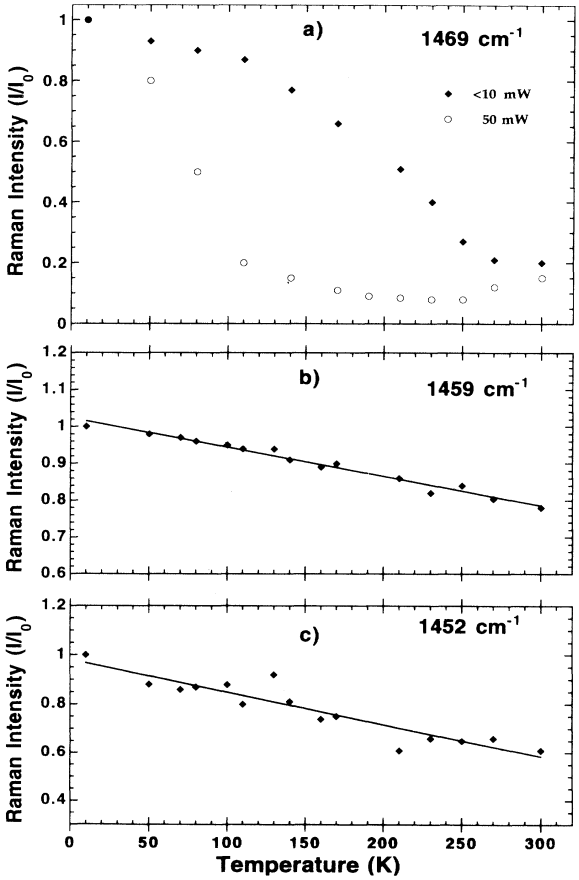

FIG. 4. Temperature dependence of the intensity of the Raman lines: (a) the 1469-cm^{-1} line under low (◆) and moderate (○) laser power, (b) the 1459-cm^{-1} line under a moderate laser power, and (c) the 1452-cm^{-1} line under a moderate laser power.

The low-temperature photoluminescence spectra performed on the same film, at the same time and under the same conditions as the Raman spectra (Fig. 6), are displayed in Fig. 7. The photoluminescence of Figs. 7(a)–7(c) is related to the Raman spectra of Figs. 6(b), 6(d), and 6(f), respectively. The profiles of these photoluminescence spectra are significantly different. (i) We observe that the peak at 1.77 eV, clearly displayed in Fig. 7(a), vanishes in the two other spectra. We have previously assigned the 1.77-eV peak, which only appears at low temperature ($T < 90$ K), to a C_{60} emission enhanced by the presence of C_{70} impurities in the solid. The effect of the C_{70} impurities is to locally distort the cluster of the neighboring C_{60} molecules, which leads to the appearance of this 1.77-eV transition.[15] The vanishing of this peak in the two other photoluminescence spectra indicates an annihilation of the effect of C_{70} impurities, suggesting a significant change in the structure of the photoluminescence centers under high strength of the laser flux. (ii) In the energy range 1.7–1.4 eV, the low-temperature photoluminescence [Fig. 7(c)] is shifted to low energy and has a broader structure with respect to the one displayed in Fig. 7(a). (iii) In the same range, the photoluminescence displayed in Fig. 7(b) appears as a weighted sum of the two others, consistently with the coexistence of the 1459- and 1469-cm^{-1} lines in the low-temperature Raman spectrum [Fig. 6(d)]. Although the two last observations can be explained following the two scenarios, obviously the former argues in favor of a phototransformation process of C_{60} upon the laser irradiation. In summary, each photoluminesence band may be related to a peculiar state of C_{60} molecules at low temperature and to different electronic properties of these states.

Finally, a Raman investigation at $T = 20$ K of the dependence of the Raman spectrum confirms, in agreement with van Loosdrecht, Bentum, and Meijer,[11] that the increase of the laser power from 1 to 100 mW resulted in the progressive appearance of a 1459-cm^{-1} Raman line, which totally replaced the 1469-cm^{-1} line at high power ($P_\lambda = 100$ mW), the decrease of the laser power restoring the 1469-cm^{-1} line. The reversible behavior of the 1459-cm^{-1} mode is totally different from those previously discussed [the present results (Fig. 6) and Refs. 1–10, 13, and 14]. In consequence, this low-temperature 1459-cm^{-1} mode, identified with C_{60} in the triplet state,[11] should not be confused with the 1459-cm^{-1} Raman spectrum associated with different forms of solid C_{60}.

3. Temperature dependence of the Raman spectrum in the high-temperature range

We have performed the dependence of the 1459-cm^{-1} Raman spectrum in the high-temperature range (300–410 K) under a moderate incident power $P_\lambda = 50$ mW. At about 410 K the spectrum drastically changes and a narrow peak at 1466 cm^{-1} dominates the spectrum [Fig. 8(a)]. On cooling the 1459-cm^{-1} line is restored at

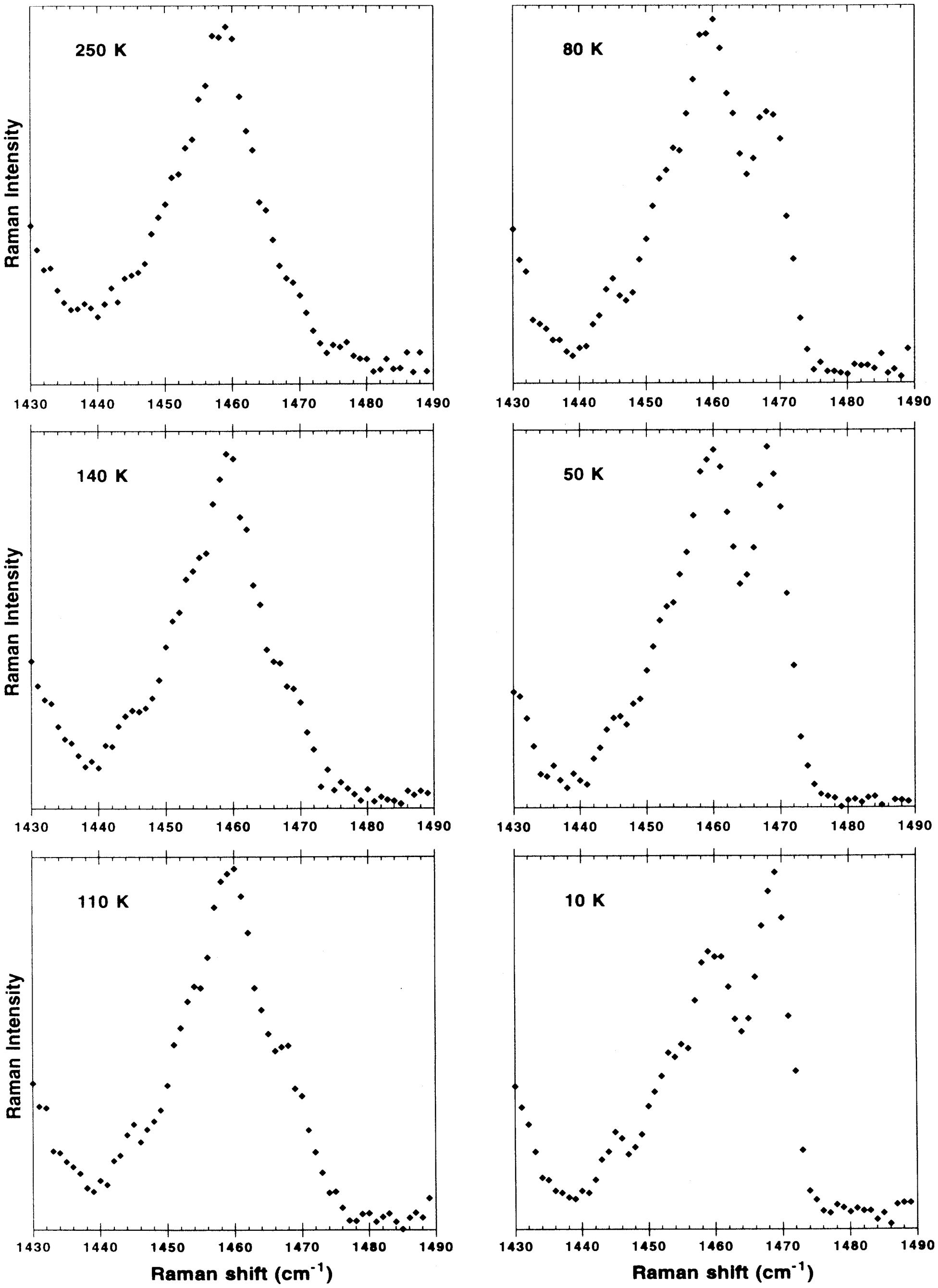

FIG. 5. Raman spectra of an oxygen-free C_{60} film on cooling under a moderate laser power $P_\lambda = 50$ mW.

around 370 K. These results can be explained, in the framework of the phototransformation of C_{60}, by considering that an annealing of the phototransformed state occurs at about 420 K and the 1466-cm^{-1} line is the intrinsic pinch mode observed at room temperature at 1469 cm^{-1} which is, as expected, shifted down when the temperature increases. The 1466-cm^{-1} Raman line measured at room temperature under high laser power ($P_\lambda = 100$ mW) [Fig. 8(b)] can be related to the local heating of the sample under the laser irradiation. In contrast to this explanation, the change of the Raman spectrum at around 420 K has been associated with a phase transition occurring at this temperature.[8] In the two explanations the Raman spectrum featured by a 1466-cm^{-1} line is associated with a complete orientationally disordered C_{60} phase at high temperature.

In summary, in the first part of this work we have obtained *on a single film* several results previously reported by different groups[1–11,13,14] and recently reviewed.[16] Consequently, we ruled out a possible sample depen-

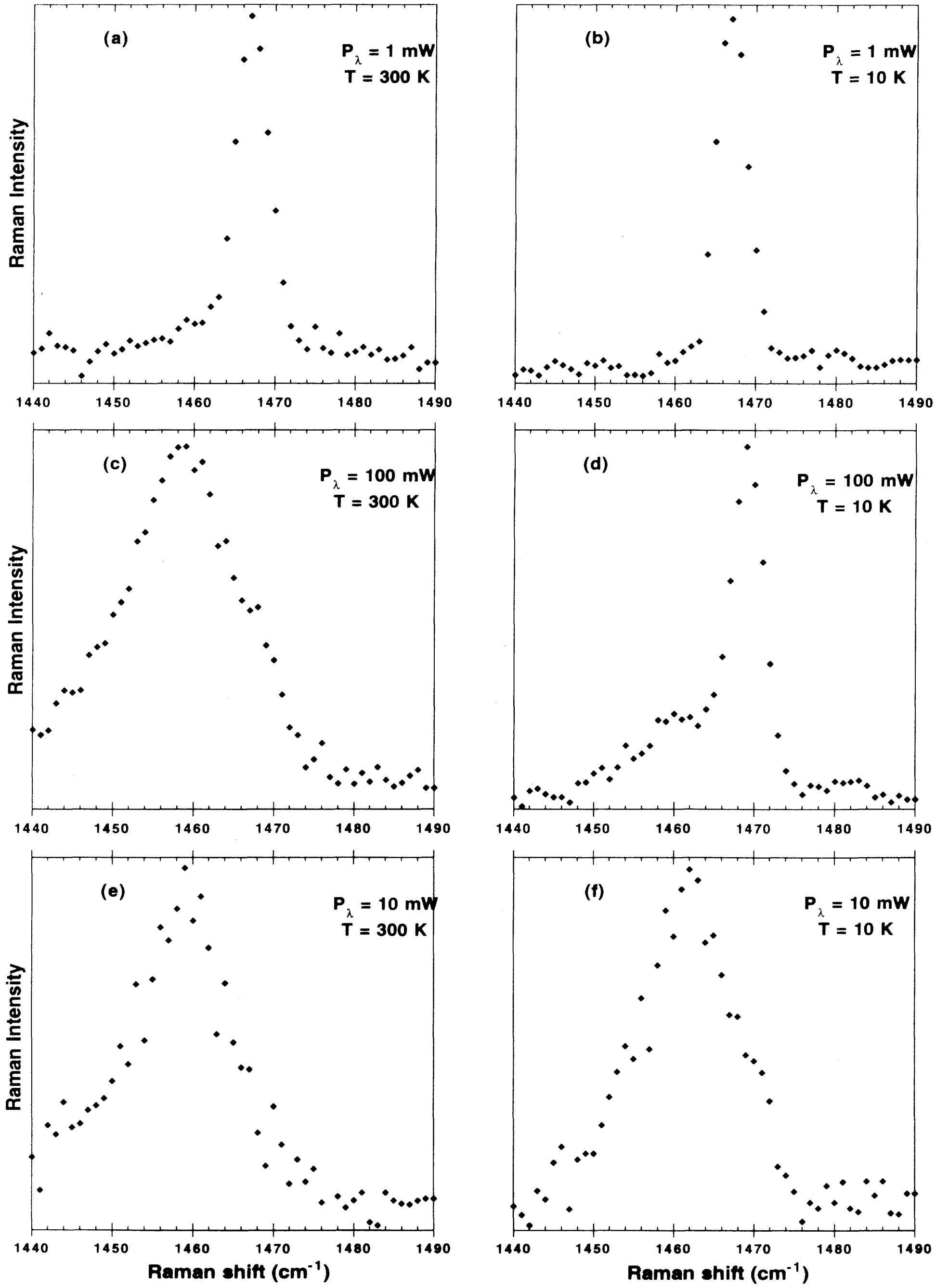

FIG. 6. Comparison between the room- and low-temperature Raman spectrum of an oxygen-free C_{60} film as a function of the laser power.

dence, which could explain the differences between these results obtained, using different experimental procedures, by these groups. We have previously underlined that all our results have been obtained on oxygen-free C_{60} films and consequently provide strong evidence that the 1469-cm^{-1} Raman spectrum is associated with oxygen-free C_{60} and the 1459-cm^{-1} Raman spectrum is induced by a strong laser light. On the other hand, we have underlined that the model proposed by Akers *et al.*[9,10] assumes unexpected behaviors for a van der Waals molecular crystal: a large shift (10 cm^{-1}) of the intramolecular mode at the order-disorder phase transition and a large range of the metastability of the high-temperature phase (150 K). In addition, the differences between the low-temperature photoluminescence bands related to the 1469-cm^{-1} low-temperature Raman spectrum and the 1459-cm^{-1} low-temperature Raman spectrum, respectively [Figs. 7(a) and 7(c)], suggest significant changes in the structure of the photoluminescent centers. These objections argue against the interpretation of all these results from the scenario proposed by Akers *et al.*,[9,10] especially the assignment of the room-temperature 1459-cm^{-1} line to a pure oxygen-free C_{60} form. The obtention of *a stable-in-air C_{60} form featured by a 1459-cm^{-1} room-temperature Raman spectrum* confirms this point of view.

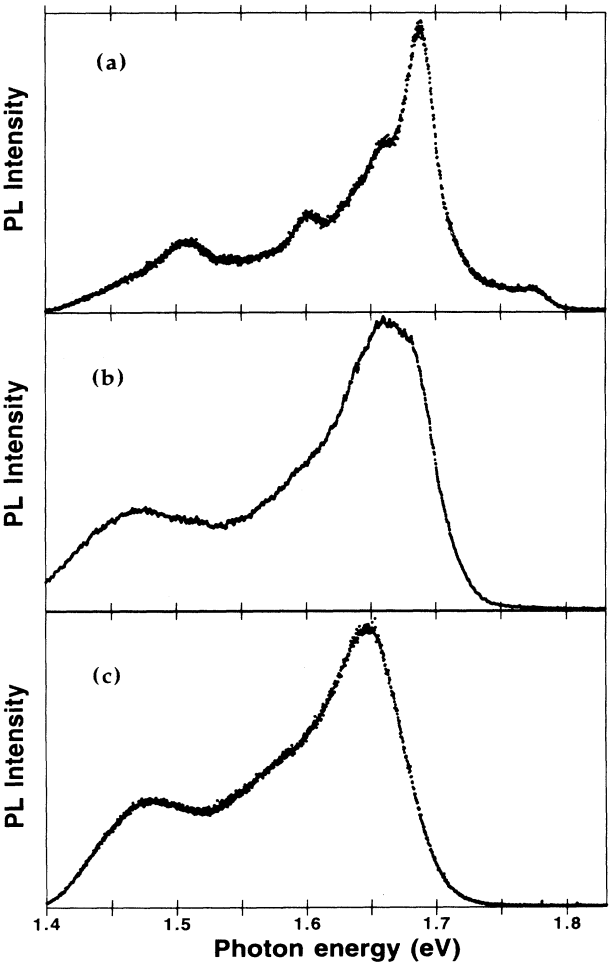

FIG. 7. Low-temperature photoluminescence of an oxygen-free C_{60} film (a) associated with the Raman spectrum displayed in Fig. 6(b), (b) associated with the Raman spectrum displayed in Fig. 6(d), and (c) associated with the Raman spectrum displayed in Fig. 6(f).

B. Stable-in-air phototransformed C_{60}

The more striking result of the preceding subsection was the restoration of the 1466-cm^{-1} line at high temperature in relation to a complete disordered state of C_{60}. Following this observation and by analogy with the behavior observed in RbC_{60} (an orientationally disordered phase at $T > 455$ K and a slow decrease of the temperature leading to a polymeric form of C_{60} at room temperature[17]), we have analyzed the changes of the Raman spectrum, performed under a moderate incident power ($P_\lambda = 10$ mW) and high vacuum, in an heating-cooling cycle 300–450–300 K. In this experiment the increase (decrease) of the temperature has been made by steps of 5 K;

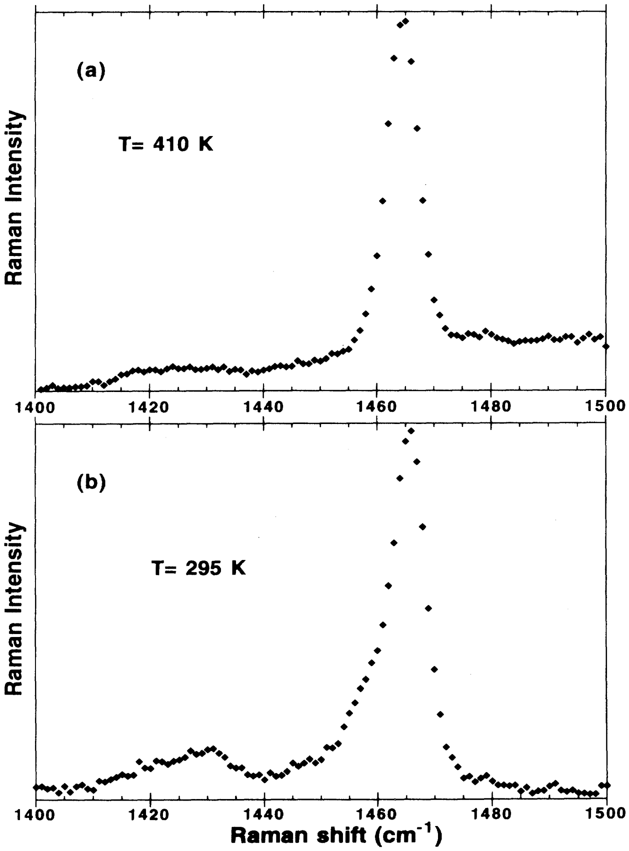

FIG. 8. Raman spectrum of an oxygen-free C_{60} film (a) under a moderate laser power $P_\lambda = 50$ mW at $T = 410$ K and (b) under a high laser power $P_\lambda = 100$ mW at $T = 295$ K.

each temperature was stabilized for 1 h before the recording of the Raman spectrum.

In Figs. 9(a)–9(c) the Raman spectra measured in the heating part of the cycle under high vacuum are displayed. The 1466-cm^{-1} line progressively emerges in the wing of the 1459-cm^{-1} line. At 420 K the spectrum drastically changes and the 1466-cm^{-1} line is dominant. We have performed a slow decrease of the temperature from 425 K to the room temperature. The 1466-cm^{-1} Raman line progressively vanishes and is replaced by the 1459-cm^{-1} Raman line [Figs. 9(d)–9(f)]. The behavior of the 1466-cm^{-1} line is hysteristic (compare the two 403 K spectra) suggesting a first-order-like transition.

At the end of the cycle, the sample is put in air at room temperature. The room-temperature Raman spectrum measured in air is displayed in Fig. 10(a). The 1459-cm^{-1} line always dominates the spectrum. The stability with the time of this in air room-temperature C_{60} form featured by the 1459-cm^{-1} Raman spectrum has been verified [Fig. 10(b)]. No evolution is observed for a period of 3 months and, in consequence, we claim that this state is stable in air. This room-temperature Raman

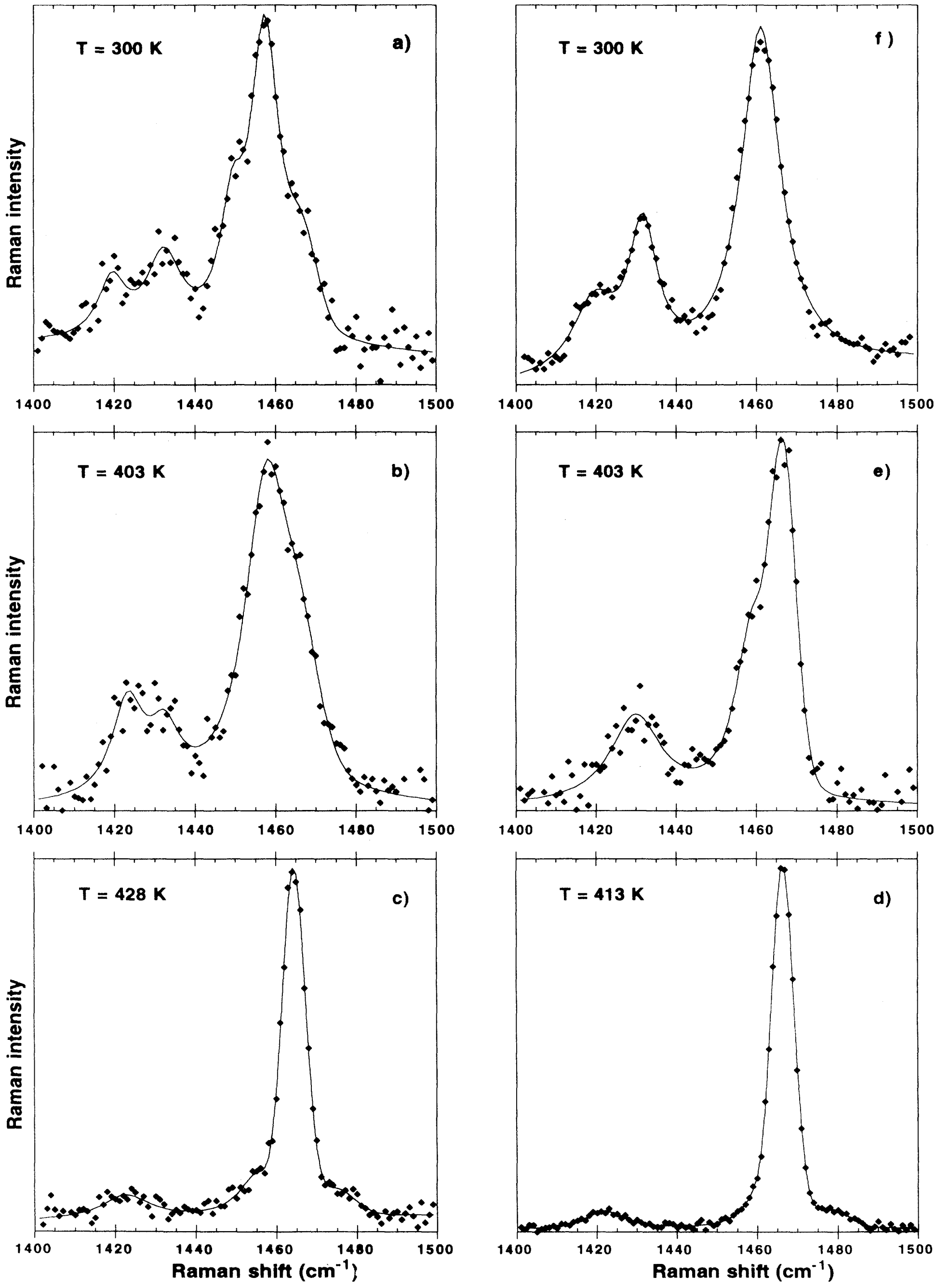

FIG. 9. Temperature dependence of the Raman spectrum in a heating-cooling cycle, 300–430–300 K, under a laser power $P_\lambda = 10$ mW.

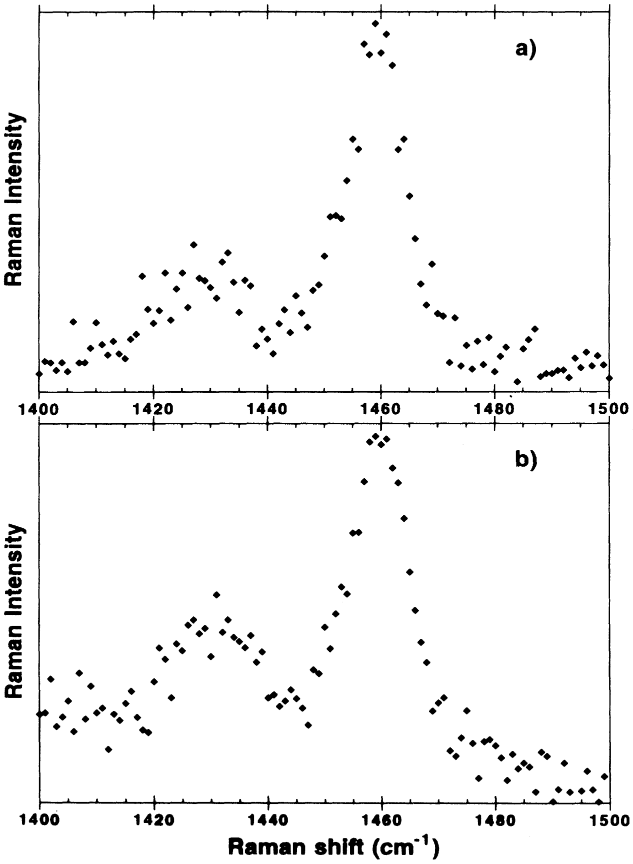

FIG. 10. Room-temperature Raman spectrum measured in air after a peculiar thermal treatment (see the text) (a) just before the exposure to air and (b) after 3 months of exposure to air.

spectrum is close to the one measured in high vacuum upon a high strength of the laser flux [Fig. 9(f) and Refs. 2 and 5–7] The analogy between these two room-temperature Raman spectra suggests the identity of the two related phases. Consequently, this unambiguously demonstrates that the 1459-cm^{-1} line cannot be associated with the *oxygen-free* C_{60} form. On the other hand, it has been previously reported that the phase obtained at room temperature in high vacuum under a high incident laser power (Sec. III A 1) was not stable in air.[3,4] Assuming a complete identity between the two phases (both are featured by the 1459-cm^{-1} room-temperature Raman spectrum), this observation provides strong evidence that the peculiar thermal treatment previously described is necessary to obtain the stable-in-air phototransformed C_{60} form.

IV. CONCLUSION

Obviously, the measurements of the 1459-cm^{-1} spectrum on a film in air seems to definitively argue against the interpretation of the 1459-cm^{-1} spectrum as that of a pure oxygen-free C_{60} form.[3,4,9,10] Consequently, we conclude that all the results shown in Sec. III A of this paper can be explained in the framework of a phototransformation of C_{60} under a moderate laser power and, consequently, we confirm the assignment of the 1469-cm^{-1} Raman spectrum to the one of pure C_{60}. Our conclusions are in complete agreement with the phototransformation process of C_{60} proposed by Rao *et al.*[6] The most important result of this study has been to obtain, after a peculiar thermal history of the sample, a stable-in-air phototransformed state. The conditions to obtain this stable-in-air phototransformed state seem to be a slow decrease of the temperature from the complete disordered phase ($T > 420$ K) to the room temperature under a moderate laser power ($P_\lambda = 10$ mW). The possibility to obtain the stable-in-air phototransformed state allows one to develop more easily several measurements concerning this state, especially x-ray diffraction and transport measurements. At this time we are working to define the precise conditions to obtain this stable-in-air phototransformed state and the structural and transport properties of this state.

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