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## Enhancement of fluorescence and Raman spectroscopies of undoped C<sub>60</sub> film

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### Abstract

The spectroscopic characteristics of C<sub>60</sub> films deposited on different substrates have been investigated at room temperature. We find that the fluorescence of C<sub>60</sub> film is enhanced by the presence of a rough silver surface and also by oxygen under excitation at 5145 Å (2.41 eV) at room temperature. The enhancement of the fluorescence on the rough silver surface is mainly due to an appropriate work function of the silver surface and an external electromagnetic field induced by laser irradiation, which leads to a resonant coupling with the C<sub>60</sub> molecular dipole. The fluorescence enhancement by oxygen is interpreted as resulting from the strong reduction in symmetry of C<sub>60</sub> from I<sub>h</sub> to C<sub>2v</sub> or lower due to photooxygenation of the C<sub>60</sub> molecules. This also results in larger Jahn–Teller distortions. The kinetics of the photochemical reactions between oxygen and C<sub>60</sub> have also been obtained with an observed rate constant of magnitude about  $1.6 \times 10^{-2} \text{ s}^{-1}$  by monitoring the changes of the fluorescence and Raman spectra with the irradiation time.

### 1. Introduction

Recent advances in the production of C<sub>60</sub> [1] in large quantities have led to its detailed study. A large number of experimental and theoretical studies have been carried out to determine the structure and chemical properties of C<sub>60</sub> [2–7]. The photophysical properties of C<sub>60</sub> have also been studied by using absorption, emission, Raman and infrared spectroscopies. Arbogart et al. [8] first determined a number of important photophysical properties of C<sub>60</sub> in hexane and benzene solution. Reber et al. [9] reported absorption and fluorescence spectra of a C<sub>60</sub> film on CaF<sub>2</sub> at 20 K.

The fluorescence spectra of the C<sub>60</sub> film was also measured as a function of temperature by several groups [10]. However, the fact that the low-lying electronic transitions in C<sub>60</sub> predicted by theory are strongly forbidden makes the interpretations of emission obtained by experiments in the region of 500–800 nm ambiguous. Moreover, the problem becomes much more complicated with the incorporation of oxygen into the C<sub>60</sub> films [11–14]. Great interest still exists to determine the excited state properties of C<sub>60</sub> molecules using luminescence, absorption and Raman scattering, especially together with the effect of the incorporating of oxygen.

In this paper, we have examined the photoluminescence and Raman scattering of a C<sub>60</sub> film at room temperature using different substrates.

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We have found that not only the Raman scattering but also the fluorescence of  $C_{60}$  film on a silver surface gets stronger, in contrast to the case when silicon or quartz substrates are used. The irradiation time dependence of the fluorescence spectra and Raman scattering of  $C_{60}$  film incorporating  $O_2$  are also discussed.

## 2. Experimental

$C_{60}$  samples were prepared by the methods of Kratschmer et al. [1], and isolated and purified by column chromatograms on alumina using mixtures of hexane and toluene as eluants. The purity of the  $C_{60}$ , checked from HPLC chromatograms, UV absorption and IR spectra, was estimated to be more than 99.5%. The solid  $C_{60}$  samples were obtained by evaporation of the column solvents.

We have deposited the  $C_{60}$  film on quartz, silicon and rough silver surfaces. The rough silver surface was constructed from polycrystalline silver wire that had been flattened. The flattened surface was polished to a mirror like finish by a sequence of polishing steps with 5.0, 0.3  $\mu\text{m}$  alumina, and each step was followed by sonication and rinsing with de-ionized water. The silver surface polished in this way likely produces a rough surface, and was further roughened by electrochemical methods similar to that in Ref. [15]. For the thin film deposition, 40 mg of purified  $C_{60}$  was loaded into a small Mo boat. The clean substrates were located approximately 20 cm from the Mo boat. After a 150°C soak cycle with the shutter closed over the substrates, the Mo boat with  $C_{60}$  molecules was heated at approximately 350°C for 30 min to evaporate  $C_{60}$  molecules at  $1.0 \times 10^{-5}$  Torr, and  $C_{60}$  was condensed onto the substrate surfaces at 100°C. The deposition rate was about 40  $\text{\AA}/\text{min}$ . The final  $C_{60}$  film thickness was about 1200  $\text{\AA}$  for all the substrates, which was determined from optical interference bands. X-ray diffraction shows essentially amorphous samples. The samples were kept in the dark with an Ar environment until used.

The Raman and luminescence studies were carried out using an  $\text{Ar}^+$  laser (Spectra Physics) at room temperature. For all the samples, 20 mW of the incident power was used and back scattering

geometries were employed. The spot size on the samples was about 300  $\mu\text{m}$  in radius. The detection system consisted of a Spex-1403 triplemate monochromator with a RCA C31034 photomultiplier tube. The time constant was always set at 1 s for Raman measurements. The slit width was 400  $\mu\text{m}$  giving a resolution of about  $2 \text{ cm}^{-1}$ . The discrimination of the Raman peaks from the 5145  $\text{\AA}$  excitation was done by comparing them with the Raman peaks obtained under 4880  $\text{\AA}$  excitation, and selecting the peaks with the same Raman shifts in both spectra. For all the Raman measurements, we used the well-known Raman cross section of Silicon to correct the  $C_{60}$  data for instrumental effects [16].

## 3. Results

The fluorescence spectra of  $C_{60}$  films on silicon and silver surfaces taken in Ar are shown in Fig. 1. The fluorescence spectra on silicon and silver surfaces at room temperature are similar with a broad peak around  $13\,545 \text{ cm}^{-1}$ , but the relative intensity of the main fluorescence peak on the silver surface is at least six times stronger than that on the silicon wafer under the same experimental conditions. So that the fluorescence of the  $C_{60}$  film on silver surface is enhanced.

Fig. 2 shows the fluorescence spectra of  $C_{60}$  films on a silver surface in an Ar and air environment. We find that the main fluorescence peak at about  $13\,545 \text{ cm}^{-1}$  in an Ar environment is much broader with some shoulders which extend to the low energy side. These probably originate from a phonon replica. The line shape of the fluorescence spectrum of a  $C_{60}$  film exposed to air is modified slightly on the low energy side. Although the main fluorescence peak is also located at about  $13\,545 \text{ cm}^{-1}$ , the fluorescence bandwidth is narrower in air than in Ar, and a new clear shoulder appears at about  $13\,295 \text{ cm}^{-1}$  when the  $C_{60}$  film is exposed to air.

Fig. 3 shows the irradiation time dependence of the fluorescence intensity of the  $C_{60}$  film on silver surface at about  $13\,545 \text{ cm}^{-1}$  in an air environment. The relative intensity shows a rapid increase with irradiation time, and reaches a maximum at

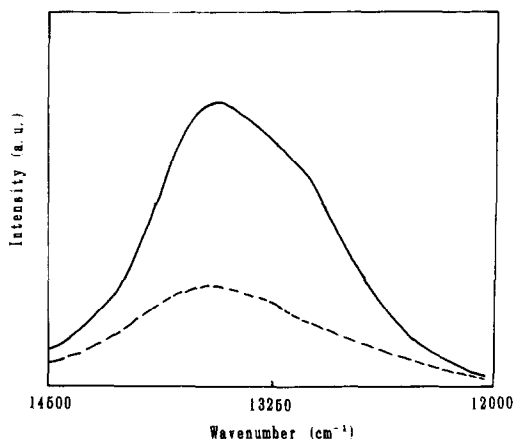


Fig. 1. Fluorescence spectra of  $C_{60}$  films deposited on a silicon wafer (---) and a silver surface (—) taken in an Ar environment at room temperature.  $\lambda_{\text{ex}} = 5145 \text{ \AA}$ .

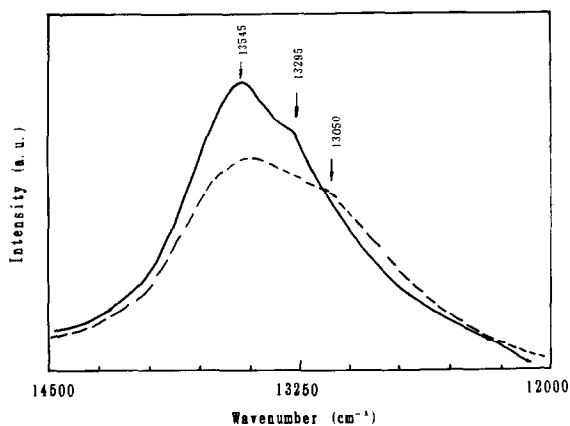


Fig. 2. Fluorescence spectra of  $C_{60}$  film deposited on a silver surface taken both in air (—) and Ar (---) environments at room temperature.  $\lambda_{\text{ex}} = 5145 \text{ \AA}$ .

about 300 s. After about 400 s, the relative intensity shows a slow linear decay with irradiation time until, at long times (about 30 min) the intensity has decreased to its original value. The linear decay above 400 s in relative intensity of fluorescence is due to the photodegradation of  $C_{60}$  molecules, an effect which is often observed in photochemistry and photobiology. Meanwhile, the fluorescence from an oxygen-free  $C_{60}$  film only shows a slow decrease with irradiation which is similar to that from oxygen-induced  $C_{60}$  film after  $t > 400$  s.

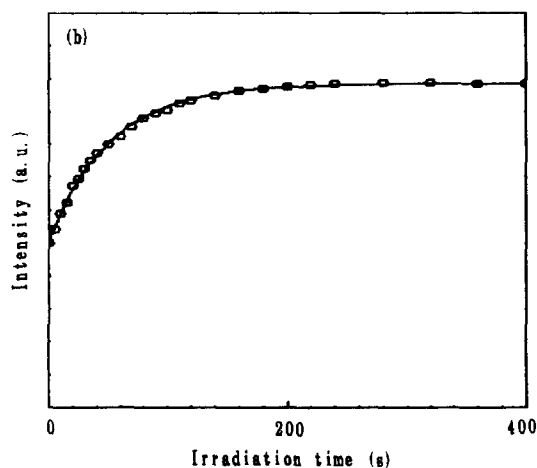
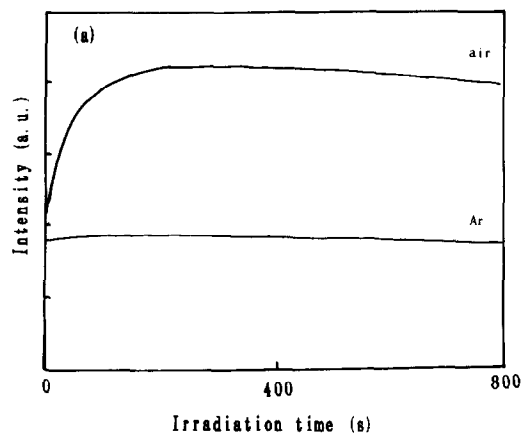


Fig. 3. Irradiation time dependence of the relative intensity of the main fluorescence peak of a  $C_{60}$  film on a silver surface at about  $13545 \text{ cm}^{-1}$  upon excitation at  $5145 \text{ \AA}$ . (a) Experimental results of the  $C_{60}$  film exposed to air (top) and Ar (down) environments, both with laser irradiation at  $5145 \text{ \AA}$ . (b) Fitted result of the curve in (a) for the  $C_{60}$  film exposed to air with the equation shown in the text. Dots represent the experimental data and the solid line represents the fitted results.

Fig. 4 shows a careful measurement of the surface enhanced Raman spectra of  $C_{60}$  films deposited on a silver surface in the region from  $1440$  to  $1480 \text{ cm}^{-1}$ , and in the region from  $200$  to  $310 \text{ cm}^{-1}$ . The  $A_g$  mode at  $1470 \text{ cm}^{-1}$  predicted by theory appears at  $1467 \text{ cm}^{-1}$  with a broad line shape on a silver surface in an Ar environment. It is surprising that when the  $C_{60}$  film is exposed to air, two new lines at  $1454$  and  $1461 \text{ cm}^{-1}$  appear. For the Raman scattering in the low frequency region, shown in Fig. 4, both Raman lines at  $256$  and

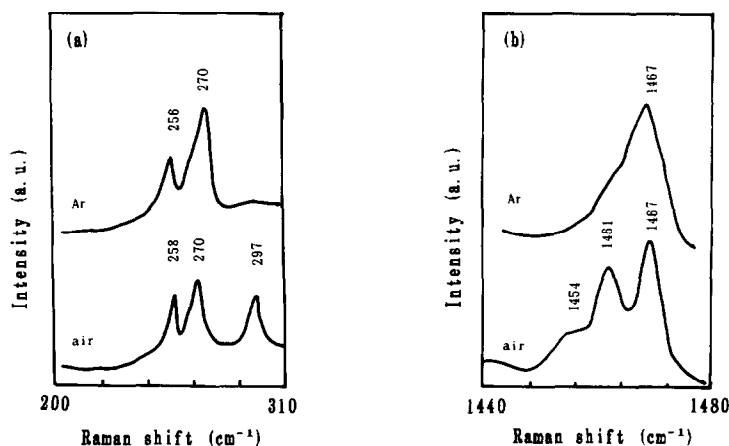


Fig. 4. Raman spectra of a  $C_{60}$  film deposited on a silver surface in the region of the  $A_g$  pentagonal pinch mode (a), and the  $H_g$  squashing mode (b), taken both in air (lower) and in Ar (top) environment.  $\lambda_{ex} = 5145 \text{ \AA}$ .

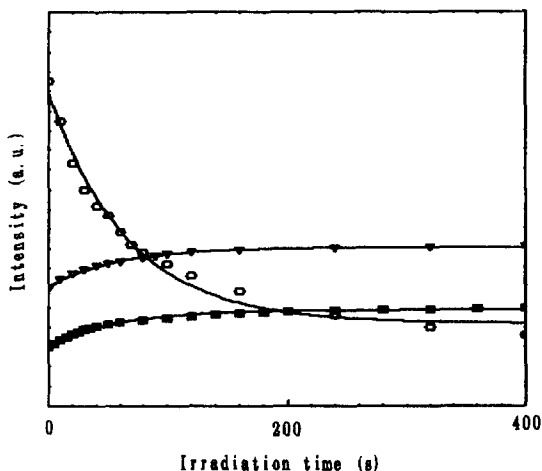


Fig. 5. Irradiation time dependence of the relative Raman intensities for the  $A_g$  pentagonal pinch mode taken in air.  $\lambda_{ex} = 5145 \text{ \AA}$ . The dots represent the experimental data, and the solid lines represent the fitted results with the equation shown in the text; (O)  $1467 \text{ cm}^{-1}$ , ( $\Delta$ )  $1461 \text{ cm}^{-1}$ , ( $\blacksquare$ )  $1454 \text{ cm}^{-1}$ .

$270 \text{ cm}^{-1}$  have commonly been observed for  $C_{60}$  films exposed to air or Ar environments, and a weak Raman line appears at  $297 \text{ cm}^{-1}$  only with air exposure. Meanwhile, the relative intensities of these three Raman lines obviously change with irradiation time at the excitation wavelength of  $5145 \text{ \AA}$  (20 mW). Fig. 5 shows the significant time

dependent changes of the relative intensities of these three Raman lines. It is interesting to note in Fig. 5 that, the intensity of  $1467 \text{ cm}^{-1}$  Raman mode decreases with irradiation time, and that of other two Raman lines at  $1454$  and  $1461 \text{ cm}^{-1}$  increase with the irradiation time.

#### 4. Discussion

The effect of incorporation of  $O_2$  into  $C_{60}$  material is of interest. The oxygen is reversibly incorporated into  $C_{60}$  without light, but the fact that it is irreversible for the oxidation process when the sample is exposed to light and air, indicates all the changes must be irradiation induced. Creegan et al. [17] synthesized and characterized the first fullerene expoxide of  $C_{60}O$  via photooxidation of  $C_{60}$  in benzene and suggested that the photooxygenation was very effective. Wood et al. [18] also noted earlier that photolysis of a crude fullerene mixture gave increased amounts of  $C_{60}O$  and  $C_{70}O$  accompanied by higher oxides  $C_{60}O_n$  ( $n = 2-5$ ). On the other hand, the oxygen may enhance S-T absorption at the lower energy region above  $500 \text{ nm}$ , which has been verified by Leach et al. [19].

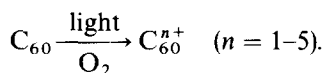
As described in the above section, we find both the rough silver surface and oxygen may enhance the fluorescence of the  $C_{60}$  film. Under identical

excitation conditions, the fluorescence is much stronger for the air-free  $C_{60}$  film on a silver surface than that on a silicon wafer (see Fig. 1) and some other substrates (data not shown). In fact, if the emitting dipole of  $C_{60}$  molecules couples well to a radiative electromagnetic resonance of the substrate surface by excitation, the emission will be enhanced [20,21]. The enhancement mechanism may be interpreted as: (1) an external electromagnetic field from the silver surface induced by laser irradiation (2.41 eV), may lead to a splitting of the degenerate  $T_{2g}$  state which results in breaking the symmetry forbidden transition from  $T_{2g}$  to ground state  $A_g$ , where the energy difference between  $1T_{2g}$  and ground state  $A_g$  is about 1.9–2.0 eV, in this case, the  $1T_{2g}$  may be taken as an effective lowest excited states, and/or (2) the difference in energy between the work function of the silver (4.8 eV) and the ionization energy (6.8 eV) [22,23] of  $C_{60}$  is coincidentally equal to the energy level of this excited state, about 2.0 eV. For these reasons, the molecular orbital populated by the excitation process may be resonant with the filled state of the silver. As a result, the electron in silver can jump into the hole formed in the molecules by the excitation process and can simultaneously eject the excited electron from  $C_{60}$  molecules. We have also checked the fluorescence properties of  $C_{60}$  films deposited on rough gold and aluminum surfaces where the work functions for gold and aluminum are 5.2 and 4.2 eV, respectively. The enhancement of fluorescence is much weaker for  $C_{60}$  film on gold and aluminum surfaces than that of silver surface. Obviously, the silver surface must be a more effective resonator for  $C_{60}$  molecules than the others. Such a result suggests that the emission effectiveness will be increased when we chose silver as the electrode for light-emitting device utilizing  $C_{60}$  material.

On the other hand, each  $C_{60}$  molecule rotates freely at room temperature. The interaction among the  $C_{60}$  molecules will be weak enough to transfer the excitation to other molecules. Therefore, it is not surprising that the emission is mainly specific to a single  $C_{60}$  molecule. However, the broad width of the fluorescence band makes it difficult to understand the fluorescence properties of  $C_{60}$ . In fact, as shown in Fig. 2, we can still distinguish at least one

shoulder, which is superimposed on the main fluorescence peak for the air-free  $C_{60}$  film deposited on a silver surface. The separation in energy between the main fluorescence peak at about  $13545\text{ cm}^{-1}$  and the clear shoulder at about  $13050\text{ cm}^{-1}$  is approximately  $495\text{ cm}^{-1}$ , which is very close to the energy of the Raman active phonon in  $C_{60}$  at  $497\text{ cm}^{-1}$  ( $A_g$  symmetric breathing motion). Therefore, the fluorescence must be associated with a phonon processes. Meanwhile, for the  $C_{60}$  film exposed to air, instead of the shoulder at about  $13050\text{ cm}^{-1}$  in an Ar environment, a new clear shoulder appears at about  $13295\text{ cm}^{-1}$ . The separation between these two positions is close to the energy of the Raman mode at about  $270\text{ cm}^{-1}$  ( $H_g$  squashing mode), which is strongly involved in the Jahn–Teller distortion of the lowest excited singlet state  $S_1$  [2,19].

Furthermore, as shown in Fig. 3, the fluorescence intensity increases with continuous irradiation for about 300 s when the  $C_{60}$  film is exposed to an air environment, and then enters a relatively stable state, where the fluorescence intensity is about two times larger in air than that in Ar. Zhou et al. [24] confirmed that most of the oxygen was located in the “near-surface” region of the film without photo-assistance using the alpha back scattering spectrum, and significant oxygen-uptake in deep bulk was observed when the film was exposed to light. Several groups have noticed that the chemical reaction of  $C_{60}$  in solution and in the solid state with oxygen needs light irradiation [17,18,24–27]. Therefore we suggest that the interaction between oxygen and  $C_{60}$  molecules must occur as a kinetic process induced by irradiation which might be described as follows:



For the rapid increase of fluorescence intensity at the initial stage of irradiation (within 400 s), this kinetics can be described by a first-order kinetic equation as:

$$F(t) = F(0) + F[1 - \exp(-k_F t)], \quad (1)$$

where  $k_F$  is the rate constant obtained as about  $1.9 \times 10^{-2}\text{ s}^{-1}$  by fitting the curve in Fig. 3(a) with

Eq. (1). The fitted result is shown in Fig. 3(b). The fact that the fluorescence is enhanced by irradiating the  $C_{60}$  film in air indicates that oxygen may play an important role in deforming spherical  $C_{60}$  fullerene towards an ellipsoidal shape. Our results support Creegan's conclusion [17] that a part of  $C_{60}$  molecules has changed to  $C_{60}O$  and/or higher oxides  $C_{60}O_n$  ( $n = 1-5$ ) by photooxygenation within the initial stage of irradiation. The  $I_h$  symmetry of the isolated  $C_{60}$  molecule therefore may be transformed into  $C_{2v}$  symmetry. This enhancement may result from the transfer of the energy to charge and some chemical reactions between  $C_{60}$  and  $O_2$  induced by irradiation, which causes the strong Jahn–Teller distortions, and removes the degeneracy. Therefore, the selection rule will change to some extent, and a part of transitions become possible, such as  $S_1 \rightarrow S_0$ ,  $S_1 \rightarrow T_1$  and  $T_1 \rightarrow S_0$  transitions which were predicted by Leach et al. [19]. The fluorescence obtained in this case must contain the contribution of the phosphorescence, since it has rather high quantum yield close to one [8]. The fluorescence spectrum (see Fig. 2) shows a clear shoulder at about  $13\,295\text{ cm}^{-1}$  superimposed on the main fluorescence peak at about  $13\,545\text{ cm}^{-1}$ , where the separation in energy between them is rather close to the  $H_g$  squashing mode at about  $270\text{ cm}^{-1}$ . This mode at  $270\text{ cm}^{-1}$  in pure  $C_{60}$  was shown to be involved in the Jahn–Teller distortion in the lowest excited state  $1T_{2g}$  [2]. The following Raman measurements further clarify this point.

Therefore, we can conclude that the fluorescence enhancement by a silver surface may be due to a film–metal interaction from a radiative field resonance near the silver surface, and the fluorescence enhancement by oxygen may be due to vibronic and spin–orbit perturbations induced by the  $C_{60}$ –oxygen reaction with irradiation; the effect of oxygen at least lowers the symmetry of the  $C_{60}$  molecules.

We now turn to the Raman scattering results with the influence of oxygen. Many works have been done on the Raman spectra of  $C_{60}$  molecules [13, 15, 28]. Duclos et al. [13] firstly considered the influence of oxygen on the  $A_g$  mode at  $1470\text{ cm}^{-1}$ , and thought the strongest Raman peak at  $1467\text{ cm}^{-1}$  was not intrinsic to pure  $C_{60}$ . In fact,

the two main modes at  $1470\text{ cm}^{-1}$  for the  $A_g$  pentagonal pinch and at  $274\text{ cm}^{-1}$  for the  $H_g$  squashing mode were known to be the most sensitive microscopic probe of the valency of  $C_{60}$  molecules with its environment [29, 30]. As shown in Fig. 4, the appearance of the  $270\text{ cm}^{-1}$  mode may be due to the solid state effect which preserves the symmetry conditions of the isolated  $C_{60}$  molecules, while the mode at  $256\text{ cm}^{-1}$  is expected to originate from the Jahn–Teller distortion upon excitation. The fact that the Raman line at  $297\text{ cm}^{-1}$  appears only in air (see Fig. 4) indicates that oxygen may cause the larger Jahn–Teller distortion upon excitation. In the high frequency region, it is located at  $1467\text{ cm}^{-1}$  with a broad line shape for the  $A_g$  pentagonal pinch mode of our pristine  $C_{60}$  film in an Ar atmosphere. The broadening of this Raman peak for the  $C_{60}$  film on a silver surface is due to the interaction between the  $C_{60}$  film and the silver surface. In fact, sufficiently thick films will also exhibit bulk properties for the  $C_{60}$  molecules far from the interface, but for very thin films, characteristics of two-dimensional systems are expected. In our case, for the amorphous  $C_{60}$  film with thickness of  $1200\text{ \AA}$ , the bulk properties must also exist, and the whole film may show an orientational disorder states, since each  $C_{60}$  molecule rapidly rotates at room temperature. When the film was exposed to air, the oxygen was located in the “near-surface” region of the film without irradiation, and quickly permeated the whole depth of the  $C_{60}$  films, reacting with the  $C_{60}$  molecules, under irradiation. At the same time, two new Raman lines appear at  $1454$  and  $1461\text{ cm}^{-1}$ . As compared to the  $A_g$  mode in alkali-metal-doped  $C_{60}$  [31, 32], we assume both anionic and cationic  $C_{60}$  has the same symmetrical properties and retains the essential electronic and structural properties of  $C_{60}$ . The two new modes at  $1461$  and  $1454\text{ cm}^{-1}$  may be interpreted as evidence for a change in the electronic structure of  $C_{60}$  as  $C_{60}^{1+}$  and  $C_{60}^{2+}$ , due to an oxidation of the  $C_{60}$  film.

The time dependent change of Raman intensity at  $1467\text{ cm}^{-1}$  with irradiation may also be best fitted by a first-order reaction kinetic equation as:

$$R(t) = R(0) + R \exp(-k_R t), \quad (2)$$

where  $k_R$  is the rate constant which can be obtained as about  $1.4 \times 10^{-2}\text{ s}^{-1}$ . The other two Raman lines

at 1461 and 1454  $\text{cm}^{-1}$  can also commonly be given by the equation as:

$$R(t) = R(0) + R[1 - \exp(-k_R t)], \quad (3)$$

where the rate constants  $k_R$  were fitted as about  $1.7 \times 10^{-2}$  and  $1.6 \times 10^{-2} \text{ s}^{-1}$  for the Raman lines at 1461 and 1454  $\text{cm}^{-1}$ , respectively. These fitted results are shown in Fig. 5. From the fitted results we find that the rate constants for the changes of these Raman lines are very similar with an order of magnitude of about  $1.6 \times 10^{-2} \text{ s}^{-1}$ , within experimental error. The rate constant for the changes of these Raman lines are also in good agreement with that for the changes of the fluorescence intensity. This rate constant may be taken as the reaction rate for oxygen incorporation into the  $\text{C}_{60}$  film, at least in some sense. Recently, Creegan et al. [17] have synthesized the first fullerene epoxide of  $\text{C}_{60}\text{O}$  by photooxygenation, and found that extensive oxidation and fragmentation of  $\text{C}_{60}$  is also induced by uv irradiation in the presence of oxygen. Meanwhile, since the fullerene of  $\text{C}_{60}\text{O}$  has  $\text{C}_2$  symmetry which derives from oxidation of one of the 30 equivalent  $\text{C}_{60}$  double bonds [17], it is not surprising that the  $\text{A}_g$  pentagonal pinch mode at 1467  $\text{cm}^{-1}$  and the  $\text{H}_g$  squashing mode at 270  $\text{cm}^{-1}$  are split into three Raman lines, respectively in an oxygenated  $\text{C}_{60}$  film. This also strongly suggests that photooxygenation may transform the soccer ball ( $\text{I}_h$  symmetry) into a rugby ball ( $\text{C}_{2v}$  or lower symmetry).

## 5. Conclusion

The fluorescence of  $\text{C}_{60}$  film may be enhanced on a rough silver surface. The enhancement has been tentatively interpreted as a resonance emission of  $\text{C}_{60}$  molecules, which results from an external electromagnetic field from the silver surface induced by laser irradiation as well as an appropriate work function of silver surface matched very well with the conduction band of the  $\text{C}_{60}$  film. Exposure of this  $\text{C}_{60}$  film to air at room temperature, leads to a fluorescence intensity which shows a rapid irradiation time-dependent increase in the initial stage (about 300s), and after about 400s, it shows a slow linear decay under continuous illumination. This indicates that at room temperature, oxygen may

play an important role in deforming spherical  $\text{C}_{60}$  fullerene towards an ellipsoidal shape through reaction with  $\text{C}_{60}$  molecules. Further supports for this point is given by the changes of Raman frequency for the  $\text{H}_g$  squashing mode at about 270  $\text{cm}^{-1}$  and  $\text{A}_g$  pentagonal pinch mode at about 1467  $\text{cm}^{-1}$  induced by oxygen and irradiation. The dynamics of the photooxygenation of the  $\text{C}_{60}$  film in air have also been obtained by monitoring the changes of the fluorescence and Raman spectra with the irradiation time. The rate constant has been obtained within an order of magnitude as about  $1.6 \times 10^{-2} \text{ s}^{-1}$  for the dynamics of the reaction between oxygen and  $\text{C}_{60}$  in an air environment. The photochemical reactions between  $\text{C}_{60}$  and oxygen are first-order reaction kinetic processes.

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