

26 June 1998

Chemical Physics Letters 290 (1998) 125-130

CHEMICAL PHYSICS LETTERS

On the nature of the laser irradiation induced reversible softening of phonon modes in C_{60} single crystals

K.P. Meletov^a, E. Liarokapis^b, J. Arvanitidis^c, K. Papagelis^c, D. Palles^b, G.A. Kourouklis^{d,*}, S. Ves^c

^a Institute of the Solid State Physics RAS, Chernogolovka, Moscow region, 142432, Russian Federation
 ^b Department of Physics, National Technical University, Athens 157 80, Greece
 ^c Physics Department, Aristotle University of Thessaloniki, GR-54006, Thessaloniki, Greece

^d Physics Division, School of Technology, Aristotle University of Thessaloniki, GR-54006, Thessaloniki, Greece

Received 19 January 1998; in final form 6 April 1998

Abstract

The average temperature rise in the laser excitation spot of the C_{60} single crystal has been determined using the Stokes to anti-Stokes integrated peak intensity ratio for the $H_g(1)$ phonon mode. The reversible softening of the $A_g(2)$ pentagon pinch mode was found to be due to the heating of the sample caused by the laser irradiation, in agreement with experimental results obtained for uniformly heated samples. These findings are in quantitative agreement with results obtained by numerical calculations of the local temperature rise, which indicates the highly non-uniform temperature distribution in the laser excitation spot associated with the small thermal conductivity of solid C_{60} . © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The response of the $A_g(2)$ pentagon pinch (PP)mode, which is the most intense band in the Raman spectrum of solid C_{60} , to a variety of perturbations has been used for the study of many diverse properties of solid fullerene and fullerene-based materials. Among them are the study of the temperature and pressure induced phase transitions, the effects caused by the intercalation of solid C_{60} with alkali metals [1-5], the dimerization processes in solid C_{60} under laser illumination and the effects caused by highpressure and -temperature treatment [6,7]. These last effects are clearly manifested by the considerable softening of the $A_{\nu}(2)$ PP-mode.

The position of the $A_g(2)$ mode, reported initially by Bethune et al. [8], in the room-temperature Raman spectrum of air-exposed C_{60} films is equal to 1469 cm⁻¹. It was also reported that the room-temperature Raman spectrum of the oxygen-free C_{60} contains a broad peak at 1459 cm⁻¹, which is more intense than the 1469 cm⁻¹ peak. The recovery of the 1469 cm⁻¹ peak is possible upon exposure of the sample to oxygen [9]. The appearance of the 1459 cm⁻¹ peak was explained, by Rao et al. [6], as the manifestation of the photoassisted dimerization of the oxygen-free C_{60} films under intense laser irradiation. It has been also shown that oxygen-exposed C_{60} films are more resistant to the laser irradiation and

^{*} Corresponding author. E-mail: gak@vergina.eng.auth.gr

^{0009-2614/98/\$19.00 © 1998} Elsevier Science B.V. All rights reserved. PII: \$0009-2614(98)00495-3

therefore, considerably higher laser power densities are needed to initiate the photodimerization reaction [6,10]. The softening of the PP-mode associated with the photodimerization of C_{60} is irreversible. The phototransformed material is stable at room temperature and can be recovered only upon heating up to temperatures higher than 420 K. When the laser illumination level is smaller than the photodimerization threshold, the PP-mode exhibits reversible softening down to 1461 cm⁻¹ upon illumination [9–11].

The reversible softening of the PP-mode, caused by laser illumination, has attracted special interest in the Raman scattering studies of solid C_{60} , especially concerning its nature [12]. Low-temperature experiments, performed at 40 K, have shown the appearance of a second wide band, downshifted by ~ 3 cm^{-1} from the 1469 cm^{-1} peak, at laser power density ~ 50 W cm⁻² [12]. Further increase of the laser power density leads to the gradual softening of this low-frequency component and rapid increase of its intensity, which, for the beam profile used in Ref. [12], becomes irreversible at laser power densities exceeding 500 W cm⁻². At the same time, the intensity of the 1469 cm⁻¹ peak goes down and disappears at 300 W cm⁻² without visible change of its peak position. The splitting and softening of the PP-mode was related to the high concentration of molecules in the lowest excited triplet state, resulting from the high absorbance of the laser radiation, the high singlet-triplet intersystem crossing and the relatively high lifetime of the excited triplet state [11-13]. It was assumed that in this case each intramolecular phonon mode will split in two Raman peaks, corresponding to the phonon frequencies of the ground and excited electronic states of the C₆₀ molecule [12]. From another point of view, the primary effect of high laser illumination is the heating of the sample, which, when combined with the loss or absorption of oxygen, may be the main reason for the phonon mode softening. The heating of the solid C_{60} under laser irradiation is possible, even at low laser power densities, due to the relatively small thermal conductivity of this material [14]. This was discussed as an alternative reason for the PP-mode softening [9,10].

We have undertaken a detailed study of the PPmode softening in the Raman spectrum of solid C_{60} as a function of laser power. Our motivation was to investigate the relation of the sample heating in the laser spot to the PP-mode softening using the relationship between the intensities of the Stokes $I_{s}(\omega)$ and anti-Stokes $I_{AS}(\omega)$ bands of the spectrum:

$$\frac{I_{\rm S}(\omega)}{I_{\rm AS}(\omega)} \left[\frac{(\omega_{\rm L} + \omega)}{(\omega_{\rm L} - \omega)} \right]^3 = \exp\left(\frac{\hbar\,\omega}{k_{\rm B}T}\right),\tag{1}$$

where T is the average temperature in the laser spot, $\omega_{\rm I}$ is the laser frequency and ω is the phonon frequency. The ratio is appropriately corrected for the ω^3 scattering efficiency factor [15]. Effects related to the frequency dependence of the optical coefficients have been ignored, as we are far from the resonance conditions. We have measured the detailed Raman spectrum of the C₆₀ single crystals in the low-frequency Stokes and anti-Stokes regions, as well as in the high-frequency region, where the PP-mode is located, at room temperature and for different laser power densities. The results obtained indicate clearly a considerable overheating of the sample in the laser spot. They agree well with the results of the temperature dependence of the PP-mode frequency obtained under a uniform bath temperature. The numerical calculations of the local temperature distribution, based on the experimental data of laser power density, absorbance and thermal conductivity of solid C_{60} , are in good agreement with the experimental results.

2. Experimental

Single crystals of fullerite were grown from the solution of C_{60} in toluene. The primary C_{60} material, with a purity better than 99%, was obtained by the Krätschmer method [16]. Data were recorded on crystals in the form of thin platelets with well-developed mirror like surfaces and dimensions ~ $300 \times 300 \times 50 \ \mu\text{m}^3$. The uniform temperature data were taken using a nitrogen gas flow cryostat stabilized to ~ 1 K, for bath temperatures up to 500 K, with the samples glued to the finger tip using a high thermal conductivity glue. The room-temperature data were taken on air-exposed freely located samples.

Raman spectra were recorded with a scrambler in the back scattering geometry at a resolution ~ 5

cm⁻¹ using a triple monochromator (DILOR XY-500) equipped with a CCD cryogenic detector system and a microscope. The power of the 514.5 nm line of an Ar⁺ laser was varied from 0.03 to 0.3 mW for a spot diameter ~ 1.25 μ m (100 × objective) and from 0.3 to ~ 2 mW for a spot diameter ~ 7.5 μm (20 × objective with flux adapter). The laser spot diameter and halfwidth are critical parameters. along with the power density, in assessing and comparing experimental results on laser beam induced effects. Throughout this Letter we have used the laser spot diameter measured at 10% of its peak intensity and the halfwidth measured at 1/e of its peak intensity. The 17976.7 cm^{-1} plasma line of the Ne lamp, located near the PP-mode frequency, was used for calibration. The data on the uniform temperature dependence were taken at the lowest laser power necessary for spectra recording. to minimize the effects of laser irradiation. By Lorentzian fittings of the spectra, the frequency peak positions were determined with an accuracy ~ 0.25 cm⁻¹ and the integrated intensities with an error < 10% of the intensity of the weakest anti-Stokes band.

3. Results and discussion

The Raman spectrum of the C_{60} single crystals, taken at room temperature, contains 10 main intramolecular modes $H_g(1)-H_g(8)$ and $A_g(1)-A_g(2)$, with frequencies close (within 2–3 cm⁻¹) to the previously determined ones [1,8]. In addition, some very weak Raman peaks were observed, which may be attributed to a second-order scattering [17]. The most intense $A_g(2)$ PP-mode, located at ~ 1467 cm⁻¹, corresponds to the out-of-phase stretching of the pentagonal and hexagonal carbon rings.

The heating of the C₆₀ crystal leads to the softening of almost all phonon modes. The increase of the uniform temperature of the sample T_{bath} to 430 K, results in the softening of the PP-mode by ~ 4.4 cm⁻¹, starting from the value of 1467.3 cm⁻¹ at T = 300 K and minimal laser power. At the same time the positions of the Raman peaks are sensitive to the laser power, the majority of the modes exhibit a softening with the increase of the laser power. At room temperature, the starting value of the PP-mode frequency decreases linearly from ~ 1465.8 cm⁻¹ at ~ 0.3 mW (and laser spot diameter ~ 7.5 μ m) down to ~ 1461.8 cm⁻¹ with increasing laser power to ~ 1.6 mW. The softening of the PP-mode under laser illumination is reversible when the laser power increases up to ~ 2 mW, above that it becomes irreversible (for an exposure time of ~ 600 s). In this case visible damage of the crystal surface, at the illumination spot region, is observed. The similarity of the PP-mode softening caused by laser power, to that caused by uniform heating of the sample, seems to be an indication of the temperature rise inside the laser illumination spot.

Fig. 1 shows the Stokes and anti-Stokes Raman bands of the three intramolecular phonon modes $H_g(1)$, $H_g(2)$ and $A_g(1)$ with frequencies 273, 435 and 495 cm⁻¹ respectively, at three different laser



Fig. 1. Raman spectra of solid C_{60} in the low-energy Stokes and anti-Stokes regions at room temperature and for different laser power densities. Laser spot diameter $d = 1.25 \ \mu$ m (halfwidth $w = 0.4 \ \mu$ m), T_{spot}^{exp} is the average temperature inside the laser spot determined from Eq. (1).

powers, 0.06, 0.15 and 0.3 mW. In the anti-Stokes region only the prominent $H_{a}(1)$ peak is clearly seen. The comparison of the integrated intensities of the strongest $H_{a}(1)$ Raman peak in the Stokes and anti-Stokes regions on the basis of Eq. (1), using the temperature T as a fitting parameter, gives the values of the average temperature T_{spot}^{\exp} in the spot. The data obtained reveal a considerable overheating of the sample within the laser illumination spot. The average temperature $T_{\rm spot}^{\rm exp}$ reaches ~ 530 K for laser power of 0.3 mW and spot diameter $\sim 1.25 \ \mu m$ (halfwidth $w = 0.4 \mu m$). The temperature at the center of the spot is even higher. These data are compatible with the visually observed damage of the crystal surface at higher laser powers, when sublimation of the material and crater creation occurs due to the extremely high overheating of the material. As discussed below, the strong temperature rise is due to the small value of the thermal conductivity, which strongly localizes the effect of the laser irradiation.

Fig. 2 shows the dependence of the PP-mode frequency on the uniform temperature of the sample $T_{\rm hath}$ (open symbols) and on the average temperature in the laser spot $T_{\text{spot}}^{\text{exp}}$ at different laser powers (solid symbols). The inset in Fig. 2 shows the PP-mode Raman peak recorded at various uniform bath temperatures. The agreement between T_{bath} and T_{spot}^{\exp} , is good and it is within the experimental error for the $T_{\rm spot}^{\rm exp}$ determination, which varies from 20 up to 50 K for different laser powers. The results obtained indicate that the average temperature of the excited crystal region inside the laser spot T_{spot}^{exp} is significantly higher than room temperature T_0 , assumed to be 300 K, and increases with laser power. The agreement between the dependencies of the PP-mode frequency on T_{bath} and T_{spot}^{\exp} indicates that the dominant effect of laser illumination is the overheating of the sample inside the laser spot. This implies also that the excited triplet state of C_{60} does not play a significant role in the softening of the PP-mode under our experimental conditions. The relatively high overheating of the fullerite, with respect to other solids, is connected primarily with the relatively small thermal conductivity of this material [14].

It may be shown that the obtained values of the laser overheating are compatible with the experimental data concerning light absorbance and thermal



Fig. 2. The dependence of the PP-mode frequency of solid C_{60} on the uniform temperature of the sample T_{bath} (open symbols) and the local temperature inside the laser excitation spot T_{spot}^{exp} (solid symbols). Inset: the PP-mode Raman peak at various temperatures for a uniformly heated sample.

conductivity of fullerite [14,18]. To check that, we have calculated the overheating temperature distribution,

$$\Delta T(R,Z) = T(R,Z) - T_0,$$

inside the laser spot, from the steady-state solution given originally by Lax [19] for constant thermal conductivity:

$$\Delta T(R,Z) = \frac{I_0 w A (1-\Re)}{K_0} \int_0^\infty d\lambda J_0(\lambda R) F(\lambda) \\ \times \left(\frac{A \exp(-\lambda Z) - \lambda \exp(-AZ)}{A^2 - \lambda^2}\right),$$
(2)

where \Re is the reflectivity, K_0 is the thermal conductivity at room temperature T_0 and R (= r/w), Z (= z/w), A (= αw) are reduced dimensionless parameters for the radius of the laser spot r, the depth z and the absorption coefficient α . In Eq. (2), $J_0(\lambda R)$

K.P. Meletov et al. / Chemical Physics Letters 290 (1998) 125-130

is the zeroth-order Bessel function and $F(\lambda)$ the corresponding Bessel transform of the laser beam profile, which was assumed to be of Gaussian shape. $I(r) = I_0 \exp(-r^2/w^2)$, where w is the beam halfwidth at 1/e of the maximum intensity I_0 . In this axial symmetry, the temperature profile depends only on the radius r and the depth z. In the above solution, the material is considered to be semi-infinite, an approximation which clearly is not valid in our case, as the crystallites are of small dimensions. However, due to the low thermal conductivity, the calculations prove that the heating is localized and follows closely the laser beam profile. The effect of the laser heating on the thermal conductivity [20] and absorption coefficient [21] have also been considered in the literature. In the present case, the thermal conductivity can be considered constant (independent of temperature) with the value of 0.4 W m⁻¹K⁻¹ above room temperature [14], though more recently even lower values for the room-temperature thermal conductivity have been reported [22]. The optical coefficients have also been considered constant (absorption 2.7 μ m⁻¹ and reflectivity 0.19 [23]) in the temperature range under consideration. The beam halfwidth w was calculated from the value given by the manufacturer of the microscope objective for the excitation wavelength at optimum focusing and for the 90% value of the total intensity. As all measurements were obtained with the microscope carefully focused, we have assumed that the real values should be close to the optimum ones, i.e. $w = 0.4 \ \mu m$ for the 100 \times magnification and 2.5 μ m for the 20 \times magnification.

The results of the temperature rise calculations are presented in Fig. 3. The inset in Fig. 3 shows the calculated temperature profiles inside the laser spot for three different laser powers 0.38, 1.15 and 1.50 mW and laser spot diameter $d = 7.5 \,\mu\text{m}$ as obtained from Eq. (2). They indicate that the temperature distribution in the spot is highly non-uniform and the maximum temperature $T_{(0,0)}$ at the center may be as high as 290 K above room temperature for 1.50 mW and $w = 2.5 \,\mu\text{m}$ (inset, Fig. 3). The ratio of the Stokes to anti-Stokes integrated intensities of the PP-mode bands has been calculated from the temperature distribution inside the laser spot (Eq. (2)), the cross-sections of the two components [15] and the temperature dependencies of the phonon frequency



Fig. 3. The temperature in the laser excitation spot as a function of the effective laser power. Solid symbols: experimental data determined from the Stokes to anti-Stokes peak intensity ratio for the $H_g(1)$ phonon mode. Solid line: the maximum temperature $T_{(0,0)}$ at the center (r = 0) of the laser spot and at zero depth (z = 0). Dashed line: theoretical prediction T_{spot}^{calc} for the average temperature. Inset: the calculated temperature profiles within the excitation spot for three different laser powers 0.38, 1.15 and 1.50 mW. Laser spot diameter ~ 7.5 μ m, calculations based on Eq. (2).

(Fig. 2) and width. From the calculated Stokes to anti-Stokes intensity ratio an average temperature $T_{\text{spot}}^{\text{calc}}$ is obtained (Fig. 3, dashed line). The temperatures in Fig. 3 are plotted as functions of the effective laser power, the ratio of the laser power to the spot radius. The reason for using this quantity is that, for low thermal conductivity, the temperature rise is roughly proportional to this quantity [19–21], which can be defined as an effective power. This scaling of the laser power to the laser spot radius is meaningful because it facilitates the comparison of experimental results obtained under different experimental parameters. According to van Loosdrecht et al. [12] an irreversible spectral change has been observed for power densities > 500 W cm⁻², which is equivalent to ~ 2.4 W cm⁻¹ (spot radius 15 μ m). This effective power is of the same order of magnitude as in our case. The data points in Fig. 3 indicate the experimental results for the average temperature T_{spot}^{exp} as obtained from the ratio of the Stokes and anti-Stokes components of the H_g(1) phonon mode. The agreement between experimental data for the average temperature T_{spot}^{exp} and the theoretical prediction T_{spot}^{calc} is good despite the fact that no adjustable parameters were used in the calculations.

4. Conclusions

The reversible softening of the PP-mode in the Raman spectrum of fullerite C_{60} under laser illumination is related to the mean temperature rise in the spot, estimated on the basis of the experimental Raman spectra in the Stokes and anti-Stokes regions. The experimental dependence of the PP-mode frequency on the uniform temperature of the sample agrees well with the dependence of the PP-mode frequency on the mean temperature in the laser spot. The numerical calculations of the local temperature in the laser spot, based on the experimental data of laser power density, optical absorption and thermal conductivity of solid C_{60} , are in good agreement with the experimental results.

Acknowledgements

Work partially supported by the General Secretariat for Research and Technology, Greece, Grant No. 96-1214, Russian Foundation for Basic Research, Grant No. 96-02-17489, Russian State Program "Fullerenes and Atomic Clusters", Grant No. 97-016 and NATO CRG No. 972317. KPM acknowledges the support and hospitality of the Laboratory of Physics, Physics Division, School of Technology, Aristotle University of Thessaloniki, during the course of this work.

References

- P.H.M. van Loosdrecht, P.J.M. van Bentum, G. Meijer, Phys. Rev. Lett. 68 (1992) 1176.
- [2] N. Chandrabhas, M.N. Shashikala, D.V.S. Muthy, A.K. Sood, C.N.R. Rao, Chem. Phys. Lett. 197 (1992) 319.
- [3] K.P. Meletov, D. Christofilos, G.A. Kourouklis, S. Ves, Chem. Phys. Lett. 236 (1995) 265.
- [4] P. Zhou, K.-A. Wang, Y. Wang, P.C. Eklund, M.S. Dresselhaus, G. Dresselhaus, R.A. Jishi, Phys. Rev. B 46 (1992) 2595.
- [5] J. Winter, H. Kuzmany, Solid State Commun. 84 (1992) 935.
- [6] A.M. Rao, P. Zhou, K.-A. Wang, G.T. Hanger, J.M. Holden, Y. Wang, W.-T. Lee, X.-X. Bi, P.C. Eklund, D.S. Cornett, W.A. Duncan, I.J. Amster, Science 259 (1993) 955.
- [7] P.-A. Persson, U. Edlund, P. Jacobsson, D. Johnels, A. Soldatov, B. Sundqvist, Chem. Phys. Lett. 258 (1996) 540.
- [8] D.S. Bethune, G. Meijer, W.C. Tang, H.J. Rosen, W.G. Golden, H. Seki, C.A. Brown, M.S. de Vries, Chem. Phys. Lett. 179 (1991) 181.
- [9] Y. Hamanaka, S. Nakashima, M. Hangyo, H. Shinohara, Y. Saito, Phys. Rev. B 48 (1993) 8510.
- [10] J.L. Sauvajol, F. Brocard, Z. Hricha, A. Zahab, Phys. Rev. B 52 (1995) 14839.
- [11] P.H.M. van Loosdrecht, P.J.M. van Bentum, M.A. Verheijen, G. Meijer, Chem. Phys. Lett. 198 (1992) 587.
- [12] P.H.M. van Loosdrecht, P.J.M. van Bentum, G. Meijer, Chem. Phys. Lett. 205 (1993) 191.
- [13] P. Zhou, Z.-H. Dong, A.M. Rao, P.C. Eklund, Chem. Phys. Lett. 211 (1993) 337.
- [14] R.C. Yu, N. Tea, M.B. Salamon, D. Lorents, R. Malhotra, Phys. Rev. Lett. 68 (1992) 2050.
- [15] W. Hayes, R. Loudon, Scattering of Light by Crystals, Wiley, New York, 1978, p. 7.
- [16] W. Krätschmer, K. Fostiropoulos, D. Huffman, Chem. Phys. Lett. 170 (1990) 167.
- [17] Z.-H. Dong, P. Zhou, J.M. Holden, P.C. Eklund, M.S. Dresselhaus, G. Dresselhaus, Phys. Rev. B 48 (1993) 2862.
- [18] K.P. Meletov, V.K. Dolganov, O.V. Zharikov, I.W. Kremenskaya, Yu.A. Ossip'yan, J. Phys. (Paris) I 2 (1992) 2097.
- [19] M. Lax, J. Appl. Phys. 48 (1977) 3919.
- [20] M. Lax, Appl. Phys. Lett. 33 (1978) 786.
- [21] E. Liarokapis, Y.S. Raptis, J. Appl. Phys. 57 (1985) 5123.
- [22] O. Andersson, A. Soldatov, B. Sundquist, Phys. Rev. B 54 (1996) 3093.
- [23] M. Patrini, F. Marabelli, G. Guizzetti, M. Manfredini, C. Castoldi, P. Milani, in: K. Kadish, R. Ruoff (Eds.), Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials, The Electrochemical Society Inc., Pennington, NJ, 1994, p. 632.