



Evidence for electron charge transfer in the polyvinylpyrrolidone–C₆₀ system as seen from ESR spectra

Ilias I. Khairullin¹, Yu-Huei Chen, Lian-Pin Hwang

Department of Chemistry, National Taiwan University, and Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23-34, Taipei, Taiwan, ROC

Received 17 October 1996; in final form 7 April 1997

Abstract

At ambient temperature the polyvinylpyrrolidone–C₆₀ system shows an ESR signal with $g = 2.0003$ comparable with a previously reported g value of the C₆₀⁻ anion radical. The ESR spectrum taken at 10 K exhibits a typical anisotropic signal, which indicates that the anion radical underwent a static Jahn–Teller distortion. The electron charge transfer from polyvinylpyrrolidone to C₆₀ may account for the observed features. © 1997 Elsevier Science B.V.

1. Introduction

In conjugated polymer–C₆₀ systems, interaction between the polymer and C₆₀ often occurs through electron charge transfer (CT) usually initiated by photoexcitation [1,2]. Thus, the concept of considering C₆₀ as a weak dopant for conjugated polymers has been theoretically developed [3]. It is little known whether non-conjugated polymers may interact with C₆₀ employing such a mechanism. Nevertheless, C₆₀ is known as a good electron acceptor [4], hence CT might also be expected in a non-conjugated polymer–C₆₀ system under appropriate conditions. Recently, Yamakoshi et al. triggered attention to polyvinylpyrrolidone (PVP) employing this non-conjugated polymer for solubilization of C₆₀ into water [5]. Although the existence of an interaction between

PVP and C₆₀ is apparent, the exact mechanism still remains unclear. In our opinion, the situation might be first ascertain in condensed media, and ESR can be a good probe for CT in particular. Here we report on ESR data for the PVP–C₆₀ composite and conclude that CT takes place in the system.

2. Experimental

C₆₀ (of 99.9% purity) and PVP with average M_w ca. 40,000 were purchased from the Material and Electrochemical Research Corp. (Arizona, USA) and from Acros (New Jersey, USA), respectively. In a typical preparation, a solution of C₆₀ in toluene (10 mg, 20 ml) was added to a solution of PVP in CHCl₃ (1 g, 40 ml). The mixture was stirred intensively to obtain a transparent solution. Thereafter, the solvent was evaporated at 60°C under a dynamic vacuum of about 100 Torr. The residue was lyophilized to produce a transparent light-brown solid PVP–C₆₀

¹ On leave from Department of Thermal Physics, Uzbekistan Academy of Sciences, Katartal Str. 28, Chilanzar C, Tashkent 700135, Republic of Uzbekistan (CIS).

composite. The sample presented in this work was prepared in an inert atmosphere utilizing degassed solvents and C_{60} preheated at 300°C for 5 h in dynamic vacuum of 10^{-5} Torr. For the ESR measurement, typically 100 mg of the composite consisting of 1 mg of C_{60} was placed into a pyrex tube without exposure to air.

ESR spectra were recorded on a Bruker ESP-300E X-band ESR spectrometer. The concentration of spins per gram of C_{60} and g values were determined with reference to those of DPPH. Due to the use of a double resonator, accuracy in the determination of the g value was estimated to be $\leq 1 \times 10^{-4}$.

3. Results and discussion

The sample of PVP- C_{60} as prepared and placed in argon only exhibited signal 1 with $g = 2.0025$ and typical $\Delta H_{pp} = 2.6 \pm 0.2$ G (Fig. 1a). No other signals appeared in the spectra over the temperature range 77–300 K. Since the polymer alone did not show any signal in this temperature range, one may refer 1 to the presence of C_{60} . An integrated intensity of 1 corresponded to a concentration of spins $(0.8 \pm 0.2) \times 10^{18}$ spin/g for C_{60} . Our preheated C_{60} demonstrated a weak intrinsic signal with $g = 2.0024$ and $\Delta H_{pp} = 1.0 \pm 0.2$ G, in agreement with other reports [6–12]. The corresponding concentration of spins was $(1.0 \pm 0.2) \times 10^{16}$ spin/g. For both, an intrinsic signal in C_{60} and 1, a peak-to-peak height, I_{pp} , exhibits clear microwave saturation with a maximum at 0.1–0.5 mW (Fig. 2a). The good resemblance of parameters and microwave saturation pattern indicates a similar signal nature. An intrinsic signal in C_{60} has been earlier related to the influence of residual molecular oxygen [10,12]. Thus, we also assign 1 in the composite to C_{60} molecules associated with oxygen. To this point it seemed that PVP- C_{60} demonstrated yet another example of an ESR signal associated with the oxygen- C_{60} pair, so we had nothing particular to look at. However, further treatments brought about a dramatic transformation of the ESR spectra.

A second signal 2 with $g = 2.0003$ and $\Delta H_{pp} = 1.8 \pm 0.2$ G appeared when the tube was evacuated for a few hours at 10^{-5} Torr and then sealed off (Fig. 1b). Signal 2 continued to grow at room tem-

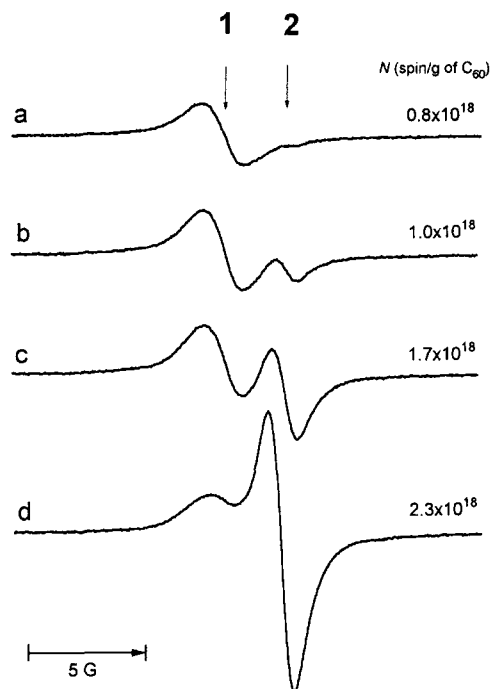


Fig. 1. The room temperature ESR spectra of PVP- C_{60} . (a) A newly prepared sample placed in argon exhibits only a signal with $g = 2.0025$ denoted 1. (b) A signal with $g = 2.0003$, denoted 2, appears at RT after evacuation of the tube at 5×10^{-5} Torr for 6 h. (c) This signal grows further at RT for 6 days in the tube sealed in vacuo. (d) Signal 2 becomes dominant after heating the sample at 60°C for 3 days. The corresponding concentrations of spins per gram for C_{60} are indicated. The spectra are recorded with the same gain, $P_{mw} = 1$ mW and $H_{mod} = 0.5$ G.

perature (RT) for several days (Fig. 1c) and increased further when we heated the sample at 60°C also for a few days (Fig. 1d). The spectra did not display such a signal when both PVP and PVP- C_{60} were heated at 60°C in air, as well as when PVP alone was heated in vacuum. Since the heating temperature was low, one could not relate 2 to polymer radicals which usually appear on pyrolysis of a polymer. However, to rule out any relation with such radicals, we heated both PVP and PVP- C_{60} at 200°C for a few hours and found a broader line with $\Delta H_{pp} = 6\text{--}7.5$ G and $g = 2.0035\text{--}2.0043$ (not presented). Undoubtedly, 2 is associated with the presence of C_{60} , and evacuation was a crucial prerequisite for its appearance. Since the signal does not get saturated at RT with P_{mw} increased up to 200 mW (Fig. 2b), its source, though related to C_{60} ,

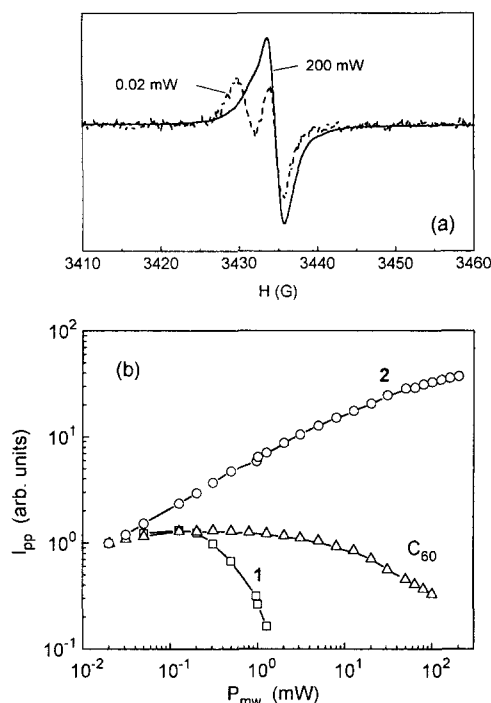


Fig. 2. The top plot (a) shows two spectra taken in PVP- C_{60} at 0.02 mW (dashed line) and 200 mW (solid line) respectively. The bottom plot (b) presents the microwave variation of the peak-to-peak intensity, I_{pp} , for 1 (square) and 2 (circle) in PVP- C_{60} and an intrinsic signal in C_{60} (triangle). Intensities are measured in arbitrary units and normalized to that taken at 0.02 mW.

differs from that of 1. The double integration of the spectrum in Fig. 1d led to a concentration of spins of $(2.3 \pm 0.3) \times 10^{18}$ spin/g for C_{60} . A rough estimate invoking the deconvolution of two Lorentzian line-shapes shows that one third of this value may relate to 1 and two thirds to 2, i.e. the concentration of spins responsible for 2 may be $(1.5 \pm 0.3) \times 10^{18}$ spin/g for C_{60} . Since the obtained value is higher than what would be expected from impurities, we classify 2 as an inherent feature of PVP- C_{60} . We detected 2 reproducibly in all the evacuated samples, which were prepared either in an inert atmosphere or in air, employing preheated or as-purchased C_{60} and regular or degassed solvents. The signal is stable and remains in the sealed samples for one year.

It has been proven in most publications that a g value of about 1.999–2.000 is a distinctive characteristic of the C_{60}^- anion radical either in solids or liquids [13–20]. This value has been related to the

quenching of the angular momentum due to the Jahn–Teller distortion of the triply degenerate T_{1u} states [13]. On the basis of those results we conclude that the main source of 2 is the C_{60}^- anion radical. The low-temperature spectra (see below) confirm our conclusion. Singh et al. have recently observed an ESR signal with comparable g value caused by C_{60}^-

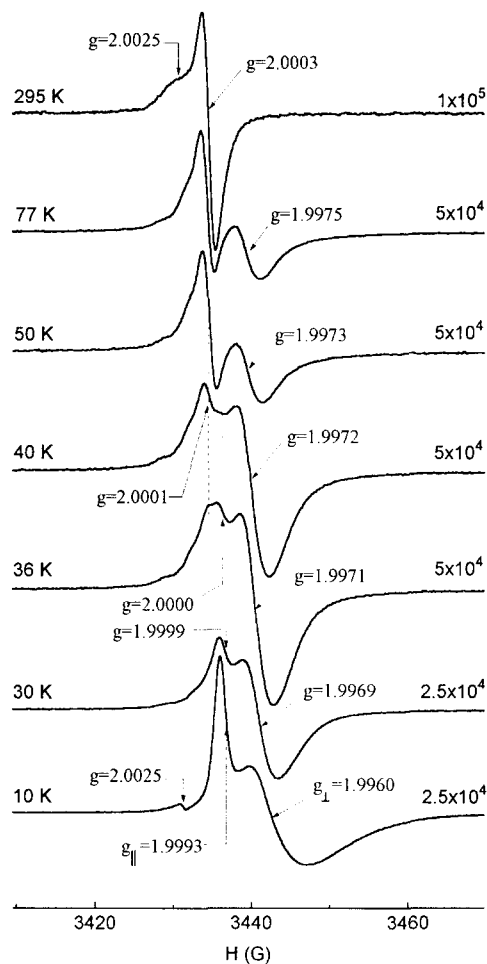


Fig. 3. The temperature variation of the ESR spectra in PVP- C_{60} . As the temperature decreases from 295 K to about 40 K, 2 reveals two distinct components. The narrow component does not shift, becomes relatively smaller and eventually disappears below 40 K. The second component appears below about 120 K, shifts toward high magnetic fields. At 10 K it evolves into a broad anisotropic signal, typical of C_{60}^- which has undergone a static Jahn–Teller distortion. Corresponding g values are indicated. Temperatures and receiver gains are shown to the left and right of each spectrum. Spectra are taken with $P_{mw} = 2$ mW and $H_{mod} = 0.5$ G.

in the oxygen– C_{60} pair [21]. Hence, we tentatively propose that the oxygen of the carbonyl group of PVP may play an important role in the donation of an electron.

Fig. 3 shows the temperature dependence of ESR spectra taken at 2 mW over the temperature range 10–295 K. The temperature variation reveals two components at the position of **2**. One of the components does not shift with decreasing temperature down to about 40 K. Meanwhile, another component starts to shift toward high magnetic fields below about 120 K and then evolves into a broad asymmetric line at lower temperatures. At 50 K, the first component is characterized by $g = 2.0001$ and $\Delta H_{pp} = 1.7 \pm 0.2$ G, while the second one has $g = 1.9975$ and $\Delta H_{pp} = 3.5 \pm 0.2$ G. Due to strong superposition it was difficult to evaluate the inherent temperature behaviors of both components. Moreover, an intensity obtained by double integration of the total spectrum followed the Curie law. During the course of the temperature evolution, a weak peak with $g = 2.0025$ and $\Delta H_{pp} = 0.7 \pm 0.2$ G emerges in the low-field wing of the spectrum. One should not confuse this weak peak with **1**; although both have virtually the same g value, the former one is narrower and does not saturate as easily as **1**. Note that at lower temperatures and given experimental settings, **1** becomes negligibly small as compared to the

other spectral components (Fig. 3), though it was still detectable down to 10 K when we used a low P_{mw} (not presented).

Below about 40 K, a sharp peak ($g = 2.0000$) emerges in the spectra near the vanishing narrow line ($g = 2.0001$) and quickly grows with decreasing in temperature (Fig. 3). At 10 K the lineshape has a strong sharp peak at low field and a broad line to high field. Khaled et al. [17] and Stinchcombe et al. [22] have reported a similar lineshape for the ESR spectrum of C_{60}^- which had undergone a static Jahn–Teller distortion. On assumption of the axially symmetrical, ellipsoidal distortion of C_{60}^- , the strong sharp peak in the 10 K spectrum in this study may represent a parallel component with $g_{\parallel} = 1.9993$, while the broad line may be a perpendicular component with $g_{\perp} = 1.9960$. A weak feature at $g = 2.0025$, which is related to C_{60}^- and observed in other works as well [17,22,23], might indicate that distortion, however, slightly differs from a simple ellipsoidal. Thus, it is evident from the obtained spectra that a complete transition from a dynamic Jahn–Teller distortion to a static distortion occurs over the temperature range 10–40 K. This is consistent with other literature reports [14,16,22].

Fig. 4 demonstrates the I_{pp} of each spectral component as a function of P_{mw} for various temperatures. The saturation pattern of the narrower line at

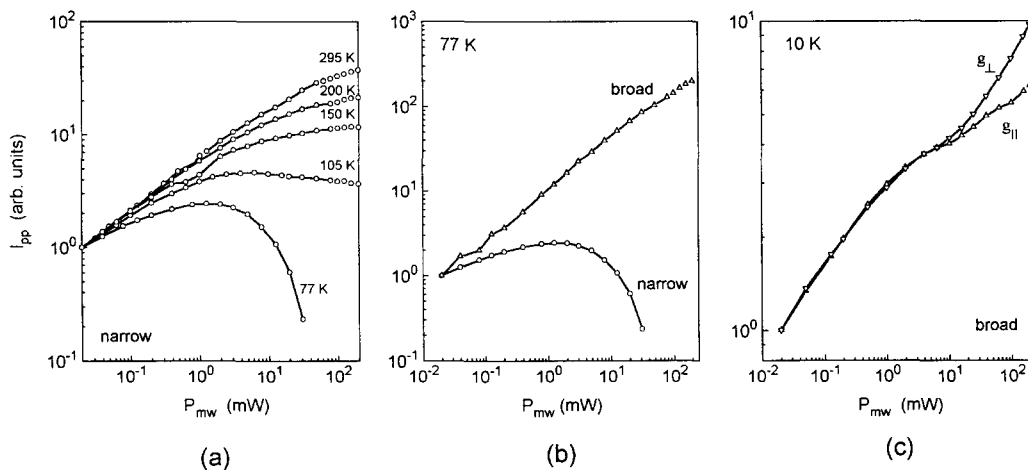


Fig. 4. Microwave variation of I_{pp} for components of the ESR spectra in PVP– C_{60} . A plot to the left (a) is for the narrow component (at position of **2**) which disappears below 40 K. A central plot (b) shows the 77 K dependence for this narrow component and its broader counterpart evolved from **2**. A plot to the left (c) presents the same dependence obtained for, respectively, a sharp and a broad component of the spectrum observed at 10 K. Since both are inherent features of the broad anisotropic signal, the corresponding intensities behave alike. For all the plots, the intensities are normalized.

the position of **2** becomes much clearer when the temperature lowers (Fig. 4a) and the broader line shifts apart (Fig. 3). The 77 K data reveal a shorter electron relaxation rate for the narrower line and a longer rate for the broader, asymmetric line (Fig. 4b). Data for the two major spectral components observed at 10 K are plotted in Fig. 4c. Since they represent inherent components of an anisotropic spectrum, the corresponding microwave saturation behaviors are alike.

At RT the linewidth is small. This can be explained by the fast reorientation of C_{60} . Consequently, a freezing motion may cause the broadening and shift in the ESR line observed below about 120 K. In the ^{13}C NMR spectra of pristine C_{60} , Yannoni et al. found that a single peak of the rapidly rotated molecule started to transform to a powder pattern at about 120 K [24]. Although the surroundings of the C_{60} molecule in polymer matrices may differ from those in pristine C_{60} , the characteristics of the motion in the absence of chemical bonds would still be similar. At 40–50 K the rotation of most molecules freezes out, but some part could still exhibit so-called pseudorotation due to the mentioned dynamic Jahn–Teller effect. The narrow line at the position of **2** may belong to such C_{60} molecules. On the other hand, this line might represent the polymer counterion. In the conjugated polymer– C_{60} system, a signal of the polymer counterion (polaron) is often stronger than that of C_{60}^- [1,2]. In the TDAE– C_{60} compound, the strongest signal comes from C_{60}^- , while the signal of the TDAE counterion is much weaker [25]. For most CT salts, the ESR spectra only exhibit a signal from the anion radical [19,26,27]. Thus, the appearance of a counterion in the ESR spectra of materials containing C_{60} is not always guaranteed. If the narrower line ($g = 2.0001$ at 50 K) is associated with the counterion, then it could perhaps be detected at lowest temperatures. In fact it disappears below 40 K (Fig. 3). This may happen if the line indeed relates to the C_{60} molecule. Nonetheless, whether our assignment of this particular component is correct or not, it does not change the fact of CT in the PVP– C_{60} system.

In conclusion, the existence of CT processes between C_{60} and PVP in the PVP– C_{60} composite is demonstrated in ESR experiments. The appropriate

conditions for CT are established only in vacuum and with annealing up to about 60°C.

Acknowledgements

This work was supported by the National Science Council of the Republic of China under Grant No. NSC 85-2113-M-001-039. I.Kh is grateful to the National Science Council for a fellowship. We thank Mr. B. Arslanov for the computer program used for the ESR data transfer.

References

- [1] N.S. Sariciftci, L. Smilowitz, A.J. Heeger, F. Wudl, *Science* 258 (1992) 1474.
- [2] L. Smilowitz, N.S. Sariciftci, R. Wu, C. Gettinger, A.J. Heeger, F. Wudl, *Phys. Rev. B* 47 (1993) 13835.
- [3] A.A. Zakhidov, I.M. Merhasin, K. Yosino, *Mol. Cryst. Liq. Cryst.* 256 (1994) 356.
- [4] Z. Yoshida, I. Dogane, H. Ikehira, T. Endo, *Chem. Phys. Lett.* 201 (1992) 4816.
- [5] Y.N. Yamakoshi, T. Yagami, K. Fukuhara, S. Sueyoshi, N. Miyata, *J. Chem. Soc., Chem. Commun.* 4 (1994) 517.
- [6] R.R. Tycko, R.C. Haddon, G. Dabbagh, S.H. Glarum, D.C. Douglass, A.M. Muzsca, *J. Phys. Chem.* 95 (1991) 518.
- [7] C.S. Yannoni, R.D. Johnson, G.D. Meijer, S. Bethune, J.R. Salem, *J. Phys. Chem.* 95 (1991) 9.
- [8] A. Howard, M. Tomietto, D.A. Wilkinson, *J. Am. Chem. Soc.* 113 (1991) 7870.
- [9] P. Byszewski, J. Stankowski, Z. Trybula, W. Kempinski, T. Zuk, *J. Mol. Struct.* 269 (1992) 175.
- [10] S. Kawata, K. Yamauchi, S. Suzuki, K. Kikuchi, H. Shiromaru, M. Katada, K. Saito, I. Ikemoto and Y. Achiba, *Chem. Lett.* (1992) 1659.
- [11] M.D. Pace, T.C. Christidis, J.J. Yin, J. Milliken, *J. Phys. Chem.* 96 (1992) 6855.
- [12] A. Bartl, L. Dunsch, U. Kirbach, B. Schandert, *Synth. Metals* 70 (1995) 1365.
- [13] T. Kato, T. Kodama, M. Oyama, S. Okazaki, T. Shida, T. Nakagawa, Y. Matsui, S. Suzuki, H. Shiromaru, K. Yamauchi, Y. Achiba, *Chem. Phys. Lett.* 186 (1991) 35.
- [14] T. Kato, T. Kodama, T. Shida, *Chem. Phys. Lett.* 205 (1993) 405.
- [15] M.A. Greaney, S.M. Gorun, *J. Phys. Chem.* 95 (1991) 7142.
- [16] D. Dubois, M.T. Jones, K.M. Kadish, *J. Am. Chem. Soc.* 114 (1992) 6446.
- [17] M.M. Khaled, R.T. Carlin, P.C. Trulove, G.R. Eaton, S.S. Eaton, *J. Am. Chem. Soc.* 116 (1994) 3465.
- [18] J. Schell-Sorokin, F. Mehran, G.R. Eaton, S.S. Eaton, A. Viehbeck, T.R. O'Toole, C.A. Brown, *Chem. Phys. Lett.* 195 (1992) 225.

- [19] P.-M. Allemand, G. Srdanov, A. Koch, K. Khemani, F. Wudl, Y. Rubin, F. Diederich, M.M. Alvarez, S.J. Anz, R.L. Whetten, *J. Am. Chem. Soc.* 113 (1991) 2780.
- [20] M. Baumgarten, A. Gügel, L. Gherghel, *Adv. Mater.* 5 (1993) 458.
- [21] K.K. Singh, T. Pradeep, D.E. Morris, L. Chen, J.V. Acrivos, *Fullerene Sci. Technol.* 4 (1996) 583.
- [22] J. Stinchcombe, A. Pénicaud, P. Bhyrappa, P.D.W. Boyd, C.A. Reed, *J. Am. Chem. Soc.* 115 (1993) 5212.
- [23] D. Dubois, K.M. Kadish, S. Flanagan, R.E. Haufler, L.P.F. Chibante, L.J. Wilson, *J. Am. Chem. Soc.* 113 (1991) 4364.
- [24] C.S. Yannoni, R.D. Johnson, G. Meijer, D.S. Bethune, J.R. Salem, *J. Phys. Chem.* 95 (1991) 9.
- [25] K. Yoshizawa, T. Sato, K. Tanaka, T. Yamabe, K. Okahara, *Chem. Phys. Lett.* 213 (1993) 498.
- [26] A. Pénicaud, A. Pérez-Benítez, R. Gleason, E. Muñoz, R. Escudero, *J. Am. Chem. Soc.* 115 (1993) 10392.
- [27] H. Moriyama, H. Kobayashi, A. Kobayashi, T. Watanabe, *J. Am. Chem. Soc.* 115 (1993) 1185.