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High-Pressure Photoluminescence Study of Fullerene C₇₀[†]J. M. Lang, Z. A. Dreger,[‡] and H. G. Drickamer**School of Chemical Sciences and The Frederick Seitz Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801**Received: March 18, 1996[⊗]*

The effect of pressure on the luminescence spectrum of the fullerene C₇₀ was measured to 100 kbar. There was a substantially linear shift on the emission envelope to lower energy by about 450 cm⁻¹ in 100 kbar. At the same time the envelope narrowed measurably. The shift is much more like that observed for olefinic compounds than for aromatics. The shift in the latter case is several times larger and distinctly nonlinear.

Since the first observation¹ and the subsequent successful synthesis² of macroscopic quantities of fullerenes C₆₀ and C₇₀, intense research activities (regarding such topics as fulleride superconductivity,³ organometallic and organic fullerene derivatives,^{4,5} and photophysical properties of fullerenes^{6–8}) have been generated on these fascinating molecules. Some of the highlights of fullerene research have been reviewed recently.^{9,10}

Although the photophysical properties of fullerenes have been extensively studied in many laboratories, most luminescence spectra of C₆₀ and C₇₀ have been observed at low temperature^{11–14} or at room temperature^{15,16} in liquid solutions at normal pressure. So far there is no report on the pressure effect on the luminescence spectra of fullerenes C₆₀ and C₇₀ in a solid polymeric medium. The purpose of this paper is to present luminescence studies to a pressure of 100 kbar for fullerene C₇₀ in poly(methyl methacrylate) (PMMA).

Experiments were also attempted with fullerene C₆₀, but, using the available exciting light and detection equipment, the intensities were too low for any quantitative measurements to be made.

Fullerene C₇₀ and PMMA were purchased from the Aldrich Chemical Co. and were used without any further purification. The samples of C₇₀ in PMMA were prepared by using a mixture of benzene and methylene chloride as solvent. The homogeneous solution was then poured onto a glass plate to form a sheet. The sample then was placed in a vacuum oven for a few days. A concentration of 10⁻⁴ mol of C₇₀/mol of PMMA monomer unit was employed.

The high pressure experiments were performed in a triangular diamond anvil cell (DAC) at room temperature (22 ± 1 °C). The details of luminescence apparatus have been described elsewhere.¹⁷ The excitation was by means of the 325 nm line of a model 3056 Omnicrome Inc. He–Cd laser. For all measurements the data were corrected for the wavelength response of various parts of the apparatus.

It has been reported¹⁵ that the spectral distribution of the excitation spectrum satisfactorily matches that of the absorption spectrum over the spectral region 250–580 nm. Visible (VIS) and ultraviolet (UV) light excitation do not show a significant difference in efficiency for producing fluorescence of C₇₀, which rules out any major dark deactivation of higher excited states bypassing the first excited S₁ state, so we used the 325 nm He–Cd laser line for excitation. Figure 1 shows fluorescence

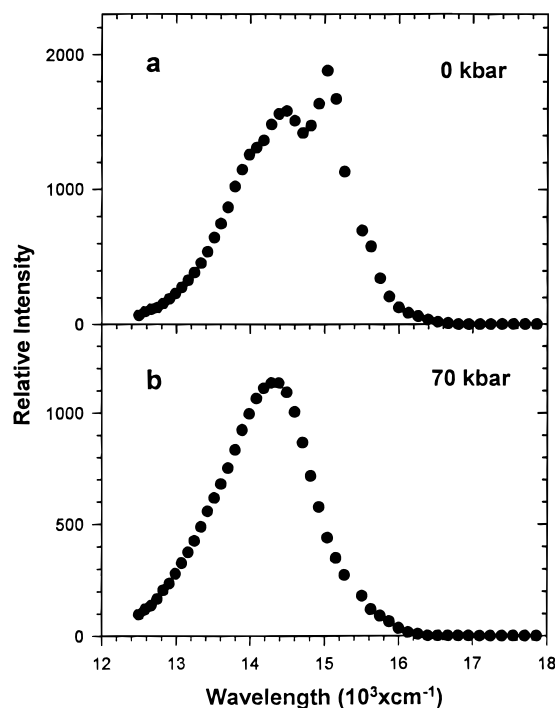


Figure 1. Fluorescence emission spectra of C₇₀ in PMMA at two different pressures. (a) 0 kbar; (b) 70 kbar.

emission spectra of C₇₀ in PMMA at 0 and 70 kbar. At atmospheric pressure the fluorescence emission spectrum of C₇₀ in PMMA which we observed is very similar to the fluorescence emission spectrum of C₇₀ in various solvents.¹⁵ The spectra consisted of a series of vibrational structure bands, which became more indistinct with increasing pressure. The relative changes of the full width at half-maximum (fwhm) for the fluorescence of C₇₀ in PMMA vs pressure are shown in Figure 2, which indicate a slight decrease up to 100 kbar. At higher pressure the indistinct vibrational structure of the fluorescence spectra is most probably due to smaller splitting and broader vibrational structure bands. It is difficult to determine the peak position at different pressures due to the slight change of peak shape. We use the average position at half-peak maximum to establish the shift. The fact that the overall width of the band envelope decreases slightly although the individual vibrational peaks broaden indicates an apparent decrease in the splitting of the vibrational components. Figure 3 shows the shifts of the fluorescence peak for C₇₀ in PMMA. The peak shifts to the red (to lower energies) with increasing pressure. The shift is about -500 cm⁻¹ up to 100 kbar.

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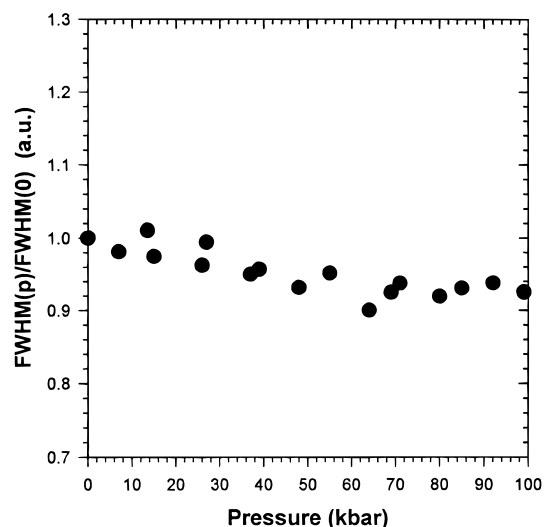


Figure 2. Pressure dependence of relative changes of the fwhm for C_{70} in PMMA.

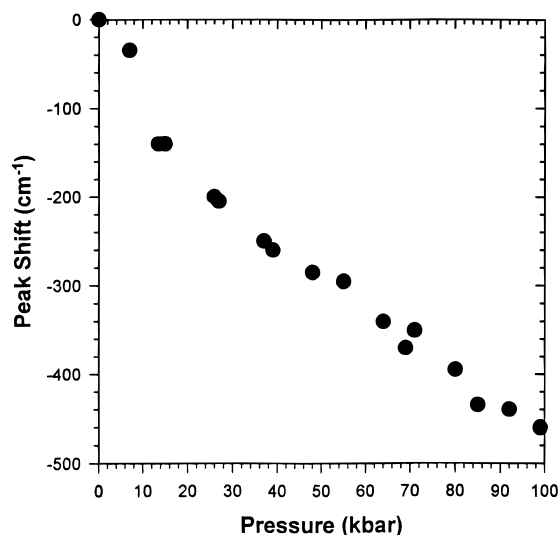


Figure 3. The shift of photoluminescence peaks vs pressure for C_{70} in PMMA.

C_{70} has the D_{5h} symmetrical ellipsoidal cage structure.¹⁸ The true chemical nature of fullerenes, however, is still generally unknown. From the study of metal complexes of fullerenes, it has been indicated that they behave chemically more like olefinic hydrocarbons.¹⁹ But the ^{13}C NMR experiments showed that the carbon atoms in fullerene C_{70} are in a pyrene-type environment.²⁰ To determine the chemical nature of C_{70} , whether more likely aromatic or olefinic, we reviewed our previous pressure studies on aromatic compounds^{21,22} such as phenanthrene and anthracene and related aromatics as well as olefinic compounds²³ such as diphenylhexatriene, and diphenyloctatetraene. For the former, the shift of fluorescence peak with pressure was very large, about -1700 cm^{-1} up to 80 kbar, while for the latter the

shift was about -300 cm^{-1} up to 40 kbar. Also, for the aromatic compounds the shift is very pressure dependent; the slope of the peak energy vs pressure curve decreases by a factor of 4–5 from low pressure to 100 kbar. As can be seen from Figure 3, the rate of peak shift for C_{70} is relatively independent of pressure, much more like the behavior of the olefinic compounds of ref 23. So from the comparison of the pressure effects on the shift of fullerene C_{70} with olefinic and aromatic compounds, our results indicate that the nature of the bonds in C_{70} is more like that of olefinic compounds.

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