Surface-enhanced Raman spectroscopy of monolayer C\textsubscript{60} Langmuir–Blodgett films

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Received 31 May 1995; accepted 10 August 1995

Abstract

The Langmuir–Blodgett (LB) films of C\textsubscript{60} mixed with stearic acid (SA) on a water subphase are deposited on optical glass substrates and their UV–Vis absorption spectra are measured. The surface-enhanced Raman spectra (SERS) of C\textsubscript{60} LB films has been observed for the first time. Silver-island film is used to obtain SERS of a well-ordered single-monolayer C\textsubscript{60} LB film. The SERS contain all fundamental Raman modes, as well as several new weak bands attributed to higher-order Raman modes as determined from factor group analysis. The enhancement of higher-order Raman scattering is probably related to C\textsubscript{60} molecular structure. The present results illustrate the potential of SRES in detecting monolayer C\textsubscript{60} LB films and in obtaining complete C\textsubscript{60} Raman spectra.

Keywords: Carbon; Langmuir–Blodgett films; Raman scattering; Surface and interface states

1. Introduction

C\textsubscript{60} has aroused intense interest because of the numerous potential applications in physics and chemistry. Theoretical and experimental research aims at better understanding the structure and properties of C\textsubscript{60}. Raman spectroscopy has proved to be an effective method to study the highly characteristic spectrum of molecular vibrations as well as the solid-state effects on the dynamical properties of C\textsubscript{60}. A large number of Raman scattering studies of C\textsubscript{60} have been published and most of the fundamental Raman-active vibration modes have been assigned [1–6]. Recently the higher-order Raman spectra have also been observed [7,8].

The Langmuir–Blodgett (LB) technique is one of the most powerful tools to form organic ultrathin films in molecular thickness. Usual materials for LB films must be amphiphilic compounds. C\textsubscript{60} is unsuitable for the LB film deposition technique because of its unique molecular structure. Early Raman scattering (RS) studies on C\textsubscript{60} involved C\textsubscript{60} powders, vapor-deposited films or single crystals. However, it has found that by mixing different matrix molecules such as arachidic acid (AA) or stearic acid (SA), uniform monolayer and multilayer C\textsubscript{60} LB films can be obtained on different substrates [9,10]. This makes it possible to investigate the physical and chemical properties of C\textsubscript{60} LB films using scanning tunnelling microscopy (STM) [10,11], high-resolution transmission electron microscopy (HRTEM) [12], and spectroscopic (UV or FTIR and Raman) techniques [10,13].

In this paper, we report SERS of C\textsubscript{60} LB films for the first time. SERS of monolayer C\textsubscript{60} LB films on an Ag island film over a frequency range of 200–2 000 cm\textsuperscript{-1} is presented. The spectrum includes two A\textsubscript{g} modes and eight H\textsubscript{g} modes as well as some extra weak modes, which can be attributed, based upon the factor group analysis, to the second-order Raman spectra of C\textsubscript{60}.

2. Experimental details

Pure C\textsubscript{60} powder used for the present study was prepared by the Kratschme–Huffman method [14]. The purity of the sample was determined to be 99% by high-performance liquid chromatography (HPLC). The LB films of the C\textsubscript{60}/SA mixture were made as follows [13]: the mixture of purified C\textsubscript{60} powder and SA in molar ratios (C\textsubscript{60}:SA) of 1:1 was dissolved in toluene using ultrasonic wave to form a C\textsubscript{60}/SA toluene solution; then one or more monolayers of the C\textsubscript{60}/SA (1:1) mixture were transferred onto optical glass substrates using a Langmuir trough apparatus (Joyce–Loebl twin-compartment trough). The addition of SA was essential for improving the qualities of the C\textsubscript{60} LB film. In SERS studies, the substrates were covered with a chemically deposited sil-
ver-island film prepared by homogeneously reducing AgNO₃ at room temperature [15]. The enhancement factor (EF) for 488.0 and 514.5 nm excitations is about 10⁶, as measured by the standard pyridine method.

The UV–Vis absorption spectra of the samples were measured with a Perkin–Elmer Lambda 5 UV–Vis spectrometer. Raman spectra were excited with lines of 488.0 and 514.5 nm of an argon ion laser. The scattered light was analysed with a SPEX-1403 double monochromator equipped with a cooled RCA 31034A photomultiplier tube and photon-counting electronics interfaced to a microcomputer. Cylindrical focusing of low laser radiation was found necessary to prevent laser-induced damage of the C₆₀ film. The resolution of the Raman spectrometer was 2 cm⁻¹.

3. Results and discussion

The UV–Vis absorption spectra of monolayer, three-layer and five-layer C₆₀ LB films on optical glass substrates were measured in the long wavelength region as shown in Fig. 1. It is readily seen that the absorbance is proportional to the number of layers, which implies that the layer accumulation has good quality. This layer-number dependence of the absorbance is similar to that of the vapor-deposited C₆₀ films, while the absorption spectra of C₆₀ LB films are in agreement with those of vapor-deposited films [16]. Hence, the matrix molecules of stearic acid do not affect the optical properties of C₆₀. On the other hand, the spectra of C₆₀ LB films are sharper than those of evaporated C₆₀ films, showing a well-defined and ordered structure.

The SERS spectrum of a monolayer C₆₀ LB film on a Ag island film using the 514.5 nm line as excitation is shown in Fig. 2. Similar spectra are obtained for the three-layer and five-layer samples. The SERS spectra of the C₆₀/SA–toluene solution, which was used to prepare the LB films, was obtained by dropping the toluene solution on Ag island film. The result is shown in Fig. 3 for comparison. The vibration properties of the single C₆₀ molecule and the C₆₀ crystal have been analysed by several authors [2–8]. The icosahedral structure I₅ of the isolated C₆₀ molecule gives rise to 46 normal modes, owing to the high symmetry. Only the two non-degenerate Aₕ modes and the eight five-fold degenerate Hₐ modes are Raman active and the four F₁₉ modes are infrared active. According to previous theoretical and experimental data [8], we identify the recorded Raman modes as shown in Fig. 2. The two strong peaks at 492 and 1468 cm⁻¹ are attributed to the molecular Aₕ modes, and peaks at 268, 430, 708, 772, 1 100, 1 250, 1 424 and 1 572 cm⁻¹ are related to all the Hₐ modes of the molecules, whereas other weak Raman modes at 350, 530, 980, 1 692, 1 746, 1 840 and 1 960 cm⁻¹ can be clearly observed in Fig. 2.

The SERS spectrum of a monolayer C₆₀ LB film on Ag island film agrees qualitatively with those of C₆₀/SA–toluene solution on Ag island film and of C₆₀–toluene solution on a Ag surface [17], as well as the Raman spectra of evaporated C₆₀ films, except for the wavenumber shift of about 2–4 cm⁻¹ toward low frequency for some bands. Compared with the Raman spectrum of C₆₀ materials, the relative intensity of SERS of C₆₀ LB films is much stronger, especially for the
two $A_g$ modes. The most outstanding feature of SERS of LB film is the high signal-to-noise ratio (SNR) the spectrum is sharp and clear, even if only a monolayer is used. As shown in Fig. 2, SERS of the C$_{60}$ LB film is complete, including all 10 fundamental modes and other weak modes, consistent with the analysis of a single C$_{60}$ molecule and of a C$_{60}$ crystal. For example, the two weak $H_g$ modes at 1 100 and 1 250 cm$^{-1}$, which are difficult to observe in spectra of C$_{60}$ powders and films or in SERS of C$_{60}$-toluene solutions, are now very clear. Another distinct feature is the appearance of several new weak modes. Finally, it is found that the linewidth of each mode in SERS of monolayer C$_{60}$ LB film is approximately 3-7 cm$^{-1}$ less than those of C$_{60}$-toluene solutions and vapor-deposited C$_{60}$ films. These features are advantageous to study of C$_{60}$.

In Fig. 2, the extra new weak modes at 350, 530, 980, 1 692, 1 746, 1 840 and 1 960 cm$^{-1}$ are obtained with a sharp Lorentzian shape, and linewidth in the range of 6-16 cm$^{-1}$. Recently, Liu et al. [8] have reported a detailed study of Raman spectra of vapor-deposited C$_{60}$ films, in which a table of the characters of combination and overtone representations in the whole I$_h$ point group was given, irrespective of Raman or IR activity. Ref. [8] shows that in the C$_{60}$ molecular crystal the second-order Raman modes are allowed by group theory, which agrees with the experimental results [7,8]. Our SERS results of monolayer C$_{60}$ LB film are in good agreement with those of Refs. [7,8] too. Notably not only the fundamental Raman modes but also the higher order modes in C$_{60}$ monolayer LB film are observed by SERS technique. High-order modes are usually very weak, e.g. the scattering intensity of the second order Raman modes is two orders of magnitude smaller than that of the fundamental modes. The appearance of the high-order modes in SERS of C$_{60}$ LB films brings a new possibility for studying the structure of C$_{60}$ LB film since their appearance comes not only from the enhancement of Ag surface, but also from the characteristics of C$_{60}$ LB film, whereas the selection rules of the high-order modes are different from those of the fundamental modes.

For both monolayer and multilayer C$_{60}$ LB films, SERS yields a similar Raman shift and relative intensity of their fundamental and high-order modes. However, the integrated intensity averaged over number of layers decreases with increasing number of layers. In both RS [1-8] and SERS most of Raman modes are at the same frequencies. These results show that each monolayer in the multilayer C$_{60}$ LB film remains of good quality in layer accumulation when deposited onto a Ag island film, and that the SERS signal comes essentially from a LB monolayer which contacts the Ag surface. Furthermore, the electromagnetic mechanism is likely to be the main enhancement mechanism owing to the fact that there is no notable frequency shift between RS and SERS.

4. Conclusion

In this work, we studied the C$_{60}$/SA LB film using UV-Vis and SERS. The results enable the following conclusions.

1. Except for improving the quality of the C$_{60}$ LB films, the matrix molecules of SA do not influence the optical and molecular vibration properties of C$_{60}$.

2. It is advantageous to use SERS of C$_{60}$ LB films of high SNR for studying not only the fundamental vibration modes, but also the enhanced higher order modes of C$_{60}$.

3. The physisorption between the LB monolayer and the metal-island film may be the main mechanism of enhancement.

References