Surface-Enhanced Raman Scattering of C_{60} and C_{70} in Gold Hydrosols

X.-C. Yang and Y. Fang*

Beijing Key Lab for Nanophotonics and Nanostructure, Department of Physics, Capital Normal University, Beijing 100037, P.R. China

Received: January 23, 2003; In Final Form: June 18, 2003

Employing pyridine molecules as media, hydrophobic C_{60} and C_{70} molecules were transported into gold hydrosols and adsorbed on the surface of gold nanoparticles, thus resulting in high-quality surface-enhanced raman scattering (SERS) spectra with enhancement factors of 8×10^4 and 6×10^5, respectively. Comparison of SERS spectra with normal Raman spectra of solid C_{60} and C_{70} indicates that these molecules absorb on gold nanoparticles by one of their pentagonal faces.

Introduction

As promising functional materials, C_{60} and C_{70} molecules have been paid extensive attention, especially in the form of thin films.[1−6] Properties of a thin film are mainly determined by its interface configuration and adsorption pattern.[7−15] Because surface-enhanced Raman scattering (SERS) uses photons as probes, which results in high-sensitivity spectra without damage to samples, revealing rich information concerning the interactions between adsorbate and base, it has become an important method of in situ investigation of thin films and interfaces.[16−20] Hydrosolution should be an ideal circumstance for this purpose, because water has no significant Raman band in the concerned range. Many Raman studies on C_{60} and C_{70} have been reported, while reports of SERS studies are dramatically rare.[21−27] A very important reason is that these two molecules have poor solubility in water.

We report for the first time the SERS spectra of C_{60} and C_{70} in hydrosols. C_{60} and C_{70} are hydrophobic molecules and have poor solubility in water. However, they dissolve much better in a polar solvent, pyridine.[28−29] In this work, C_{60}/C_{70}−pyridine solutions were added into gold hydrosols. With the help of pyridine molecules, the fullerene molecules approached gold nanoparticles and adsorbed onto them. Thus, we recorded SERS spectra that contained abundant information. We chose pyridine as solvent medium on the basis of three aspects. First, in our preliminary experiment as well as in other authors' works,[28,29] 60 and 70 fullerenes both had significant solubility in pyridine compared to that in many other solvents, so it is easy to get solutions of almost arbitrary concentrations. Second, among the limited kinds of favorable solvents, pyridine is unique for its miscibility with water. Furthermore, Raman and SERS bands of pyridine have been widely studied[30−33] and can be easily recognized and ruled out. Analyzing of the SERS spectra shows that gold nanoparticles account for a large enhancement to the Raman bands of C_{60} and C_{70}. On the basis of analyses of the activation of several inactive modes and bands' splitting, we infer that a C_{60} or C_{70} molecule is seemingly adsorbed on a gold nanoparticle by one of its pentagonal faces.

Experiment

Sample Preparation. C_{60} and C_{70} were ultrasonically dissolved in pure pyridine in advance, and the solutions were kept

* Corresponding author. E-mail: weduf@263.net.
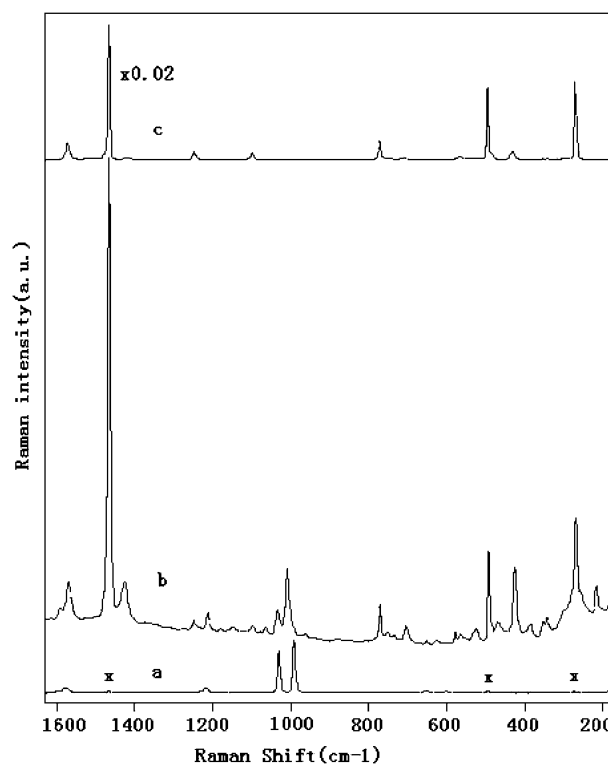
Figure 1. Raman and SERS spectra of C_{60}: (a) Raman spectrum of C_{60}−pyridine solution (peaks marked with an x are attributed to C_{60}.); (b) SERS spectrum of C_{60}−pyridine solution mixed with Au colloid of treble volume; (c) Raman spectrum of solid C_{60} for recognition reference.
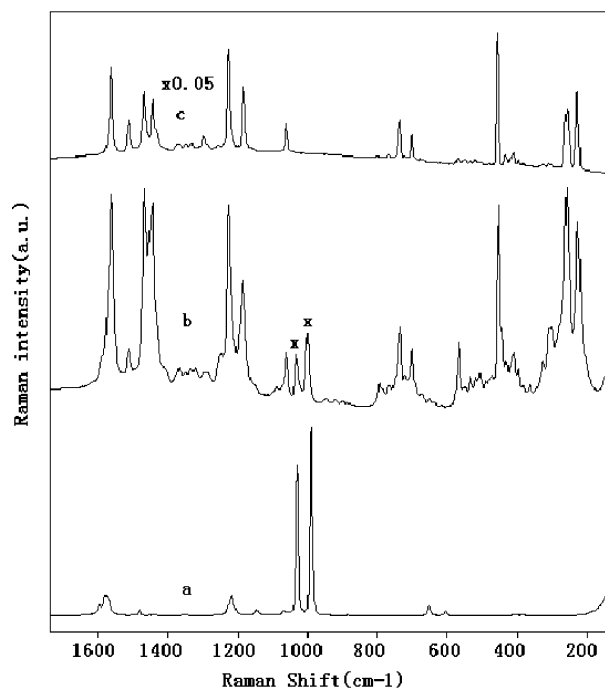
vibrating in an ultrasonic cleaning cell for at least 4 h before being taken as Raman or SERS samples. Gold hydrosols were prepared through a redox process according to Sutherland et al.[34] except that $HAuCl_4$ was substituted by $KAuCl_4$.

Raman spectra were recorded by an RFS 100/S FT-IR spectrophotometer (excited at 1064 nm). All liquid samples were under the same exciting laser power and aperture size.

Results and Discussion

FT-NIR SERS spectra of the mixture of C_{60}/C_{70}−pyridine solution and gold hydrosol give rich information (Figures 1 and 2). The ratio of pyridine solution to hydrosol in the sample

Figure 2. Raman and SERS spectra of C$_{70}$: (a) Raman spectrum of C$_{70}$−pyridine solution; (b) SERS spectrum of C$_{70}$−pyridine solution mixed with Au colloid of treble volume (peaks marked with an x are attributed to pyridine); (c) Raman spectrum of solid C$_{70}$ for recognition reference.

mixture has an interesting influence on the enhancement effect, which we wouldd like to discuss elsewhere.[35] Figure 1 shows Raman spectra of a typical set of C$_{60}$ samples: (a) Raman spectrum of C$_{60}$−pyridine solution; (b) SERS spectrum of C$_{60}$−pyridine solution mixed with gold hydrosol of treble volume; and (c) Raman spectrum of solid C$_{60}$ for recognition reference (scaled down by 50 times).

Table 1 shows attribution of the observed bands in Figure 1. As we can see, most of the stronger bands in Figure 1a are attributed to pyridine.[31−33] Only three weak bands of C$_{60}$ could be seen: H$_g$(1) (272 cm^{-1}), A$_g$(1) (496 cm^{-1}), and A$_g$(2) (1469 cm^{-1}). This is easy to understand, because, in the C$_{60}$−pyridine solution, the molar concentration of C$_{60}$ is far less than that of pyridine. In our experiment, C$_{60}$ is ultrasonically dissolved in pure pyridine. The final solution shows a dark brown color and has a C$_{60}$ solubility of 1.4 mg/mL. Such a result is a great progress compared with the work of Scrivens et al., who got a pink solution with a C$_{60}$ solubility of 0.3 mg/mL in pyridine.[29] Yet in our dark brown solution, the molar concentration of C$_{60}$ is merely around 2×10^{-3} M, while that of pyridine is around 14 M. Such a great concentration difference accounts for the intensity contrast in Figure 1a.

In the SERS spectrum of the mixture solution (Figure 1b), however, the three bands mentioned above are very strong, even stronger than the characteristic ring breathing bands (1003, 1014, and 1035 cm^{-1}) of pyridine. To evaluate the enhancement efficiency of this system, we quote a simple formula to calculate the enhancement factor:[36]

$$G = (I_{sers}n_{bulk})/(I_{Raman}n_{surf}) \qquad (1)$$

Here I_{sers} and I_{Raman} stand for the intensities of a given typical band in SERS and Raman spectra, respectively; n_{bulk} and n_{surf} stand for the number of C$_{60}$ molecules in the bulk and the number of those adsorbed on the surface of gold nanoparticles, respectively, in a unit volume of the mixture solution. Choosing

A$_g$(2) (1469 cm^{-1}) in Figure 1b as the typical band, we made out that the enhancement factor G of the pyridine−nanoparticle system for C$_{60}$ was about 8×10^4.

Although C$_{60}$ has a low molar concentration in the mixture sample solution, the contrast between SERS (Figure 1b) and normal Raman (Figure 1a) spectra indicates that a host of C$_{60}$ molecules have successfully launched on the surface of gold particles. Pyridine molecules play a crucial role in this process. Surrounded by polar pyridine molecules, the otherwise hydrophobic C$_{60}$ molecules sufficiently disperse in hydrosol, get access to gold nanoparticles, and adsorb onto them.

The SERS spectrum of C$_{60}$ reveals not only that normal Raman active modes (2A$_g$ + 8H$_g$) have been greatly enhanced but also that a number of inactive modes got activated. As can be seen in Figure 1 and Table 1, most of the newly activated bands concentrate in the 200−600 cm^{-1} range. Theoretical calculations have shown that this range is concerned with radical breathing modes of the pentagonal faces of C$_{60}$.[37] The activation pattern suggests such an adsorption image: a C$_{60}$ molecule tends to adsorb on a gold nanoparticle by one of its 12 pentagonal faces.

Splitting of several bands again gives support to such an image. According to group theory, pentagonal adsorption would result in degradation of the C$_{60}$ molecule group—from a highly symmetric I_h group to a C_{5v} group. An H$_g$ mode of the I_h group would split into three modes of the C_{5v} group with lower degeneracy (A$_1$ + E$_1$ + E$_2$), and a T$_{1u}$ mode of the I_h group would split into two modes of the C_{5v} group (A$_1$ + E$_1$). In Figure 1b we see the H$_g$ (1) band of C$_{60}$ split into three (255, 269, and 295 cm^{-1}) and the T$_{1u}$ (2) band split into two (555 and 575 cm^{-1}).

Figure 2 shows Raman spectra of a typical set of C$_{70}$ samples: (a) Raman spectrum of C$_{70}$−pyridine solution; (b) SERS spectrum of C$_{70}$−pyridine solution mixed with gold hydrosol of treble volume; and (c) Raman spectrum of solid C$_{70}$ for recognition reference (scaled down by 20 times).

Ultrasonically dissolved in pure pyridine, C$_{70}$ gets a solubility of 3 mg/mL, which is greater than that of C$_{60}$. Still, we hardly see any typical band of this rugby-like molecule in the Raman spectrum of the C$_{70}$-pyridine solution (Figure 2a). However, in the SERS spectrum (Figure 2b), many strong Raman active modes of C$_{70}$ are observed, with their relative intensities differing from that of the solid state (Figure 2c). As discussed in the case of C$_{60}$, we believe this means successful adsorption of a large number of C$_{70}$ molecules on gold nanoparticles. The bands concerned with C$_{70}$ in Figure 2b are shown in Table 2, where the bands belonging to pyridine have been kicked off.

Choosing the 254 cm^{-1} (A$_1'$) band of C$_{70}$ in Figure 2b as a typical band, by formula 1 we get an enhancement factor G of the pyridine−nanoparticle system for C$_{70}$ of about 6×10^5. Though the enhancement factor G of C$_{70}$ is much greater than that of C$_{60}$, Figure 2b does not present as much of an abundant message as in the case of Figure 1b. Even within the range 400−800 cm^{-1}, where bands are most concentrated, we cannot give accurate recognition due to widening and overlaying of the observed weak bands.

Still, we can conjecture the adsorption behavior of C$_{70}$ on gold nanoparticles. There may be a number of possible adsorption modes, each bringing about different changes to the symmetry of the C$_{70}$ molecule.

If a C$_{70}$ molecule is adsorbed on a gold surface by one of its two pentagonal "polar" faces, its molecule group would change

TABLE 1: Band Recognition of Figure 1: Their Relative Intensities[a] and Assignments

Raman bands (cm⁻¹)		SERS bands of mixture sample (cm⁻¹)	relative intensity in SERS spec	assignment[21-25,27,30-32]
solid C_{60}	C_{60}-pyridine solution			
		255	w	C_{60} $H_g(1)$
273	272(w)	269	vs	C_{60} $H_g(1)$
		295	m	C_{60} $H_g(1)$
		341	s	C_{60} $H_u(1)$
432		420	s	C_{60} $H_g(2)$
		478	m	C_{60} $G_g(1)$
496	496(w)	491	s	C_{60} $A_g(1)$
		519	s	C_{60} $T_{1u}(1)$
568		555	m	C_{60} $T_{1u}(2))$
		575	m	C_{60} $T_{1u}(2)$
	653(m)	650	m	pyridine in-plane ring deformation
710		707	m	C_{60} $H_g(3)$
		734	w	C_{60} $H_g(3)$
772		767	s	C_{60} $H_g(4)$
		963	w	C_{60} $2A_g(1)$
	992(vs)	1003	vs	pyridine symmetric ring breathing
		1014	vs	pyridine symmetric ring breathing
	1031(vs)	1035	vs	pyridine asymmetric ring breathing
	1069(w)	1066	w	pyridine in-plane C−H bending
1100		1099	m	C_{60} $H_g(5)$
	1147(w)	1153	w	pyridine in-plane C−H bending
		1184	w	C_{60} $T_{1u}(3)$
	1219(m)	1217	m	pyridine in-plane C−H bending
1250		1247	m	C_{60} $H_g(6)$
		1343	w	C_{60} $T_{1g}(3)$
1424		1422	s	C_{60} $H_g(7)/T_{1u}(4)$
1468	1468(w)	1462	vs	C_{60} $A_g(2)$
	1483(w)			pyridine ring stretching
1574		1564	s	C_{60} $H_g(8)$
	1581(m)			pyridine ring stretching
	1598(w)	1600	m	pyridine ring stretching

[a] vs, very strong; s, strong; m, medium; w, weak.

TABLE 2: Bands Belonging to C_{70} and Their Relative Intensities[a] in Figure 3b[23,38-39]

peak (cm⁻¹)	relative intensity	peak (cm⁻¹)	relative intensity
222	s	735	m
254	s	794	w
301	s	945	w
373	w	1065	m
424	w	1190	s
443	s	1229	s
454	m	1370	w
463	m	1452	s
494	w	1468	s
535	w	1513	w
567	m	1565	s
721	w		

[a] s, strong; m, medium; w, weak.

from a D_{5h} group to a C_{5v} group, and the number of Raman active modes would increase from 53 to 104 ($22A_1 + 40E_1 + 42E_2$).

If a C_{70} molecule is adsorbed on a gold surface by one of its five hexagonal faces that are parallel to its long axis, its molecule group would change from a D_{5h} group to a C_{2v} group. If a C_{70} molecule is adsorbed on a gold surface by one of its other 30 faces, its molecule group would change from a D_{5h} group to a C_{2s} group. In these two cases, the number of Raman active modes increases from 53 to 204 ($55A_1 + 48A_2 + 49B_1 + 52B_2$ in the case of a C_{2v} group or $104A' + 100A''$ in the case of a C_{2s} group).

Comparison of Figure 2b and c indicates that the SERS spectrum of the C_{70}-pyridine and gold colloid mixture solution resembles and is somewhat richer than the Raman spectrum of solid C_{70}, but it does not show much difference in the number of Raman active bands. That is to say no significant symmetry degradation and band splitting are induced due to adsorption. Hence, we infer that the most possible adsorption pattern might be the one that brings about lest symmetry change, that is, a C_{70} molecule adsorbed by one of its two "polar" pentagonal faces on the surface of a gold nanoparticle.

What is the interaction pattern between fullerene and pyridine molecules? Do they bond via the nitrogen lone-pair electrons of pyridine? No definite conclusion could be easily drawn here. With the facts in mind that among favorable fullerene solvents are CS_2, CCl_4, benzene, and toluene, while among poor solvents are *n*-hexane, *n*-decane, and acetonitrile, we conjecture that neither methyl in a linear hydrocarbon nor nitrogen lone-pair electrons in acetonitrile or pyridine seem to have any priority over the hydrogen atoms on the ring of benzene or pyridine. There might be several different schemes of bonding between fullerene and pyridine molecules, especially in the complicated environment of hydrosol. Anyway, further work may give new key(s) to this question.

What role pyridine molecules play in this course should be given thought. SERS spectra prove that, with the help of pyridine, fullerene molecules successfully landed on gold clusters. But where are the pyridine "transporters" thereafter? Do they form a diffusive mediate layer between gold nanoparticles and fullerene molecules or "modestly" retreat from the interface and wave back to the aqueous solution, leaving fullerene molecules bound to the gold surface directly? SERS spectra show a relatively slight enhancement of pyridine bands compared to Raman spectra (Figures 1 and 2) before Au colloid is added. This might be a result of balance between adsorption-induced enhancement and dilution-induced decrease in Raman

SERS of C_{60} and C_{70} in Gold Hydrosols

J. Phys. Chem. B, Vol. 107, No. 37, 2003 **10103**

intensity. So we conjecture that pyridine failed in the adsorption competition with fullerene and most pyridine molecules appear at some distance from the interface.

Conclusion

In summary, we employed pyridine molecules as "transporters" to help C_{60} and C_{70} be dissolved into hydrosol and adsorbed on gold nanoparticles; thus, we obtained high-quality SERS spectra. Calculated enhancement factors of the pyridine/nanoparticle system for C_{60} and C_{70} are as large as 8×10^4 and 6×10^5, respectively. SERS spectra contain abundant information concerning with the fullerene molecules as well as the adsorption pattern on metal surfaces, especially in the case of C_{60}. So, our work provides an effective method for obtaining SERS of hydrophobic substances.

In SERS spectra of C_{60} and C_{70} we observed a large enhancement of Raman bands and activation of many inactive modes. Comparing the SERS spectra with normal Raman spectra, we inferred that C_{60} and C_{70} molecules likely adsorbed on gold nanoparticles by one of their pentagonal faces, which brought new experimental proof for elucidating the mechanism of molecule adsorption on metal surfaces as well as that of the SERS effect itself.

References and Notes

(1) Schwedhelm, R.; et al. *Phys. Rev. B* **1998**, *58* (19), 13176.
(2) Saab, A. P.; et al. *Adv. Mater.* **1998**, *10* (6), 462.
(3) Hasegawa, S.; et al. *J. Electron Spectrosc. Relat. Phenom.* **1998**, *88−91*, 891.
(4) Nakamoto, K.; et al. *J. Chem. Educ.* **2000**, *77* (6), 775.
(5) Al-Mohamad, A.; et al. *Synth. Met.* **1999**, *104*, 39.
(6) Ganeev, R. A.; et al. *Opt. Commun.* **2000**, *185*, 473.
(7) Haddon, R. C.; et al. *Nature* **1991**, *350*, 32.
(8) Rao, A. M.; et al. *Science* **1993**, *259*, 955.
(9) Giudice, E.; et al. *Surf. Sci.* **1998**, *405*, L561.
(10) Goldoni, A.; et al. *Surf. Sci.* **1999**, *437*, 353.
(11) Swami, N.; et al. *Surf. Sci.* **1999**, *425*, 141.
(12) Kenny, D. J.; et al. *Surf. Sci.* **2000**, *447*, 126.
(13) Yase, K.; et al. *Thin Solid Films* **1998**, *331*, 131.
(14) Hou, J. G.; et al. *J. Phys.: Condens. Matter* **1998**, *10*, 9609.
(15) Manaila, R.; et al. *Fullerene Sci. Technol.* **1999**, *7* (1), 59.
(16) Kerker, M.; et al. *J. Phys. Chem.* **1984**, *88*, 3168.
(17) Okamoto, T. L.; et al. *Opt. Lett.* **2000**, *25*, 372.
(18) Rivas, L.; et al. *Langmuir* **2000**, *16*, 9722.
(19) Lecomte, S.; et al. *Langmuir* **1998**, *14*, 4373.
(20) Miao, R. C.; et al. *Acta Phys. Sinica* **1988**, *37* (11), 1870.
(21) Dong, Z. H.; et al. *Phys. Rev. B* **1993**, *48* (4), 2862.
(22) Liu, R.; et al. *Phys. Rev. B* **1992**, *45* (19), 11437.
(23) Akers, K. L.; et al. *Chem. Phys. Lett.* **1992**, *190* (6), 614.
(24) van Loosdrecht, P. H. M.; et al. *Chem. Phys. Lett.* **1992**, *198* (6), 587.
(25) Love, S. P.; et al. *Chem. Phys. Lett.* **1994**, *225*, 170.
(26) Rafailov, P. M.; et al. *Solid State Commun.* **1999**, *112*, 517.
(27) Matus, M.; et al. *Appl. Phys. A* **1993**, *56*, 241.
(28) Ruoff, R. S.; et al. *J. Phys. Chem.* **1993**, *97*, 3379.
(29) Scrivens, W. A.; et al. *J. Chem. Soc., Chem. Commun.* **1993**, 1207.
(30) Creighton, J. A.; et al. *J. Chem. Soc., Faraday Trans.* **1979**, *75*, 790.
(31) Li, W. H.; et al. *Chem. Phys. Lett.* **1999**, *305*, 303.
(32) Gu, R. A.; et al. *J. Electroanal. Chem.* **2001**, *505*, 95.
(33) Nicholson, M. A.; et al. *Vib. Spectrosc.* **2000**, *24*, 157.
(34) Sutherland, W. S.; et al. *J. Colloid Interface Sci.* **1992**, *148*, 129.
(35) Yang, X. C.; et al. *Acta Phys. Sinica*, to be submitted.
(36) Zhu, Z. H.; et al. *Acta Phys.-Chim. Sinica* **2000**, *2*, 138.
(37) Hebard, A. F. *Phys. Today* **1992**, *45*, 26.
(38) Gallagher, S. H.; et al. *J. Am. Chem. Soc.* **1997**, *119*, 4263.
(39) Wang, X. Q.; et al. *Phys. Rev. B* **1995**, *51* (13), 8656.