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Fundamental and higher-order Raman spectra of C_{60} films

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Raman spectra of C_{60} films on gold and silicon substrates have been taken over the frequency range 200–3200 cm^{-1}. Besides two A_g and eight H_g fundamental frequency modes, 16 weak peaks are observed. According to the selection rules of overtone and combination bands, most of them are attributed to the second-order Raman spectra of C_{60} molecules. A comparison of experimental results with theoretical predictions shows satisfactory agreement.

C_{60}, and the class of core all-carbon clusters,[1] has attracted much attention in the past because of their numerous potential applications in various areas of physics and chemistry. Preliminary studies on alkali-metal-doped C_{60} have shown superconductivity with T_c as high as 18 and 33 K.[2,3] Pure fullerene is presently being studied as a precursor for the nucleation of diamond thin films.[4] For these reasons, much theoretical and experimental research work has been recently performed in order to fully characterize the properties of C_{60} as well as its structure. Raman spectroscopy has proved to be a convenient method to study the highly characteristic spectrum of molecular vibrations and the solid-state effects on the dynamical properties of C_{60}. Although Raman-scattering studies of C_{60} have been reported extensively and most of the fundamental Raman-active vibrational modes have been assigned,[5–13] the identification of some weak peaks at 532, 564, 980, 1692, and 1850 cm^{-1} has been reported,[9–13] and no vibrational spectra of C_{60} up to 3200 cm^{-1} have been reported so far.

In this paper, we present a Raman study of thin C_{60} films on Au and Si substrates over a large frequency range of 200–3200 cm^{-1} to investigate the fundamental and additional vibration modes. Besides two A_g modes and eight H_g modes, 16 weak bands are observed in both samples. Based upon the factor group analysis, most of them are attributed to the second-order Raman spectra of C_{60}.

Samples of C_{60} studied here were prepared by the well-known Krätschmer-Huffman method[1] and purified by high-performance liquid chromatography to 99.9%. Thin films were generated by sublimating the purified C_{60} powder on Au and Si single-crystal substrates at 400 °C in a vacuum of 10 Torr. The films were designed to grow along the [111] direction of substrates, which ensures a high quality sample. Microscopically, numerous crystallites can be found, the size of them being in the range from 1–2 μm to 20–30 μm. All samples are about 200 nm in thickness.

Raman spectra were collected in back-scattering geometry at room temperature using a Spex 1403 double-grating monochrometer with a C31034 photomultiplier tube. Cylindrical focusing of low laser radiation was found necessary to prevent laser-induce damage to the C_{60} films. The sources for excitation were argon laser lines with 488.0 and 514.5 nm, and instrument resolution was 2 cm^{-1}.

Figures 1 and 2 show Raman spectra of the C_{60} film on gold substrate using 514.5 nm laser radiation, which are similar to the spectra of a silicon substrate sample except for some increase in intensities of the Raman peaks. Five strong peaks at 272, 496, 1424, 1468, and 1574 cm^{-1} and twenty-one weak peaks at 432, 532, 566, 710, 772, 980, 1100, 1250, 1692, and 1838 cm^{-1} can be clearly observed. For comparison with previous theoretical and experimental data,[6,9,12,14] see Table I. According to the report of Bethune and co-workers[6–9] the two strong peaks at 1468 and 496 cm^{-1} can be attributed to the molecular A_g modes, and peaks at 272, 432, 710, 772, 1100, 1250, 1424, and 1574 cm^{-1} are related to all the H_g modes of the molecules. Other weak Raman features at 3148, 2998, 2936, 2846, 2676, 2348, 2330, 2196, 2134, 2014, 1962, 1838, 1692, 980, 566, and 532 cm^{-1} have sharp Lorentz shapes, their linewidth is in the range of 6–20 cm^{-1}.

The vibration properties of the single C_{60} molecule and crystal have been analyzed by several authors.[15,16] The icosahedral structure I_h of the isolated molecule gives rise to 46 normal modes:

$$\Gamma C_{60} = 2A_g + 3F_{1g} + 4F_{2g} + 6G_g + 8H_g + A_u + 4F_{1u} + 5F_{2u} + 6G_u + 7H_u$$

among which only the two nondegenerate A_g modes and eight fivefold degenerate H_g modes are Raman active, and the four $F_{1\mu}$ modes are infrared active. In the solid state the crystal field influences the vibrational properties as well as the selection rules. Since, for soft molecular

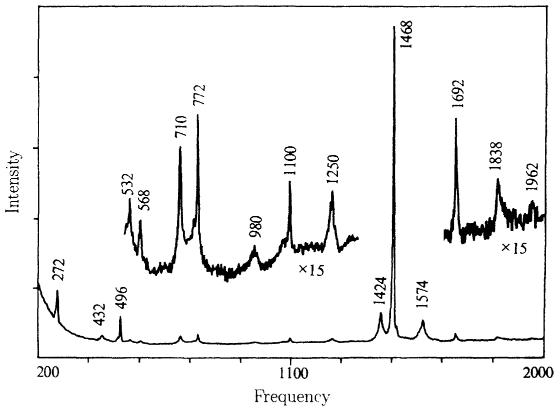

FIG. 1. Raman spectrum of C_{60} film on gold substrate over the frequency range 200–2000 cm^{-1}.

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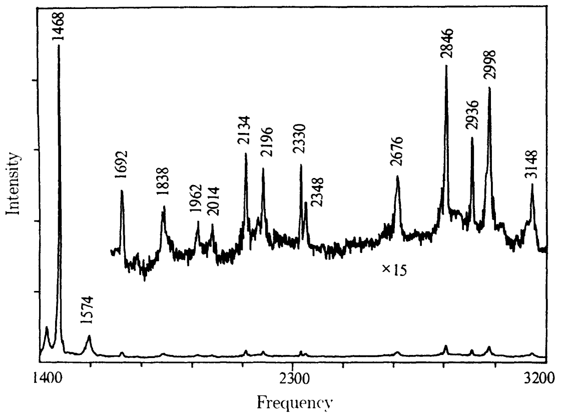

FIG. 2. Raman spectrum of C_{60} film on gold substrate over the frequency range 1400–3200 cm^{-1}.

crystal C_{60}, molecules are bonded by weak van der Waals forces and the individual molecular structure is well defined, one expects that the frequencies of the internal modes are only slightly influenced, yielding small shifts and splitting of these modes. The crystal field effectively lowers the symmetry of the molecules and, therefore, some of the molecular inactive modes will become active in the solid state.[12] For example, the additional peaks at 532, 568, and 980 cm^{-1}, which appeared in Fig. 1, are also observed by other researchers;[9,12] comparing with previous theoretical and experimental results,[12,14] they can be tentatively attributed to F_{2g}, F_{1u}, and F_{1g} silent modes of C_{60} molecules. Other high-frequency internal vibration modes are observed. One cannot relate them to the first-order silent modes since their frequencies are too high. These peaks are more likely to be the second-order Raman-active modes.

The Raman or infrared spectrum of a molecular crystal may contain numerous combination and overtone bands arising from anharmonicity effect. The combination bands belong to representations that are obtained by the direct product of those representations to which belong the internal fundamental vibrations of molecule whose sum of frequencies gives the observed frequency.[17] In the cases of overtone bands, the characters of vibration representations are given by[18,19]

$$\chi_f^2(\hat{R})=[\chi_f(\hat{R})]^2\ , \quad f=1\ ,$$

$$\chi_f^2(\hat{R})=\tfrac{1}{2}\{[\chi_f(\hat{R})]^2+\chi_f(\hat{R}^2)\}\ , \quad f\geq 2\ ,$$

TABLE I. Experimental and theoretical vibration frequencies (cm^{-1}) of C_{60}.

Raman[a]	IR Raman[b]	Raman[c]	Calculated[d]	Raman[a]	IR Raman[b]	Raman[c]	Calculated[d]
272	273	272	269 (H_g)		1183 (IR)		1208 (F_{1u})
		350	361 (H_u)				1212 (F_{2u})
			367 (F_{2u})	1250	1250	1250	1217 (H_g)
			385 (G_u)				1327 (G_u)
432	437	432	439 (H_g)				1346 (F_{1g})
496	496	492	492 (A_g)				1351 (F_{2g})
			498 (G_g)				1375 (G_g)
			501 (F_{1g})				1385 (H_u)
	527 (IR)		505 (F_{1u})	1424	1428	1426	1401 (H_g)
532		532	541 (F_{2g})				1413 (G_u)
			543 (H_u)		1428 (IR)		1450 (F_{1u})
568	577 (IR)	564	589 (F_{1u})	1468	1470	1468	1468 (A_g)
			626 (G_g)				1521 (G_g)
			677 (F_{2u})				1552 (H_u)
			700 (H_u)				1575 (F_{2u})
710	710	710	708 (H_g)	1574	1575	1572	1575 (H_g)
772	774	770	788 (H_g)	1692		1692	
			789 (G_u)	1838		1850	
			801 (H_u)	1962			
			805 (G_g)	2014			
			847 (F_{2g})	2134			
			929 (G_u)	2196			
			931 (F_{2g})	2330			
			961 (G_u)	2348			
980			981 (F_{1g})	2676			
			1025 (F_{2u})	2846			
			1056 (G_g)	2936			
1100	1099	1100	1102 (H_g)	2998			
			1129 (H_u)	3148			
			1142 (A_u)				

[a] This work.
[b] Reference 6.
[c] Reference 9.
[d] Reference 14.

where the quantity $\chi_f(\hat{R})$ denotes the character of f-fold degenerate irreducible representation (ir) for the symmetry operation $\hat{R}$ of the point group, and $\chi_f^2(\hat{R})$ the character of the reducible representation of the first-order overtone whose fundamental vibrations belong to f-fold degenerate ir. These bands have well-defined frequencies and their width is of the same order of magnitude as those of the fundamental bands. In these cases, predictions from selection rules based on the factor groups are generally sufficient.[17]

The characters for combination and overtone vibration representations in the I_h point group are listed in Table II along with the linear combinations of ir decomposed from the corresponding representations. From Table II, one can see for C_{60} molecular crystals that the second-order Raman spectra are allowed by group theory, which is in agreement with the experimental results (see Table III).

To confirm the above explanation for high-frequency features, polarized Raman experiments of C_{60} films have been performed over the range of 2700–3200 cm^{-1}. From Fig. 3, one can see that the C_{60} lines at 2846, 2998, and 3148 cm^{-1} are depolarized, while the line at 2936 cm^{-1} is seen to be highly polarized, strongly suggesting that the associated mode is totally symmetric.

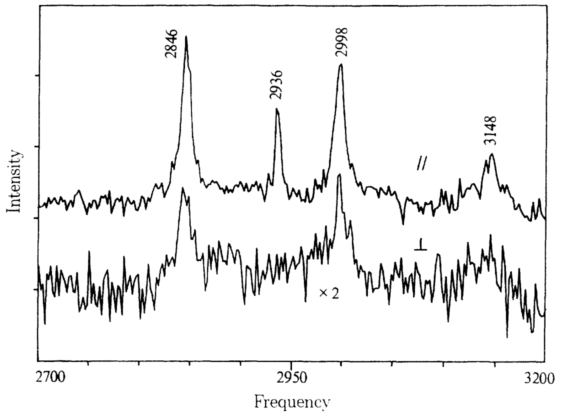

FIG. 3. Polarized Raman spectra of C_{60} film on gold substrate over the frequency range of 2700–3200 cm^{-1}.

Why do these combination and overtone bands show characters of a line and not a continuous spectrum? The answer to this question can be drawn from the distinction between internal and external frequencies. The general

TABLE II. Characters for combination and overtone vibration representations in the I_h point group, where $[\Gamma]^2$ represents the first-order overtone of Γ ir, $\tau=(1+\sqrt{5})/2$.

I_h	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$	i	$12S_{10}^3$	$12S_{10}$	$20S_3$	$15\sigma_v$	
$[A_g]^2$	1	1	1	1	1	1	1	1	1	1	$\Longrightarrow A_g$
$[F_{1g}]^2$	6	1	1	0	2	6	1	1	0	2	$\Longrightarrow A_g+H_g$
$[F_{2g}]^2$	6	1	1	0	2	6	1	1	0	2	$\Longrightarrow A_g+H_g$
$[G_g]^2$	10	0	0	1	2	10	0	0	1	2	$\Longrightarrow A_g+G_g+H_g$
$[H_g]^2$	15	0	0	0	3	15	0	0	0	3	$\Longrightarrow A_g+G_g+2H_g$
$[A_u]^2$	1	1	1	1	1	1	1	1	1	1	$\Longrightarrow A_g$
$[F_{1u}]^2$	6	1	1	0	2	6	1	1	0	2	$\Longrightarrow A_g+H_g$
$[F_{2u}]^2$	6	1	1	0	2	6	1	1	0	2	$\Longrightarrow A_g+H_g$
$[G_u]^2$	10	0	0	1	2	10	0	0	1	2	$\Longrightarrow A_g+G_g+H_g$
$[H_u]^2$	15	0	0	0	3	15	0	0	0	3	$\Longrightarrow A_g+G_g+2H_g$
$A_g\otimes A_g$	1	1	1	1	1	1	1	1	1	1	$\Longrightarrow A_g$
$A_g\otimes H_g$	5	0	0	-1	1	5	0	0	-1	1	$\Longrightarrow H_g$
$F_{1g}\otimes F_{1g}$	9	$1+\tau$	$2-\tau$	0	1	9	$1+\tau$	$2-\tau$	0	1	$\Longrightarrow A_g+F_{1g}+H_g$
$F_{1g}\otimes F_{2g}$	9	-1	-1	0	1	9	-1	-1	0	1	$\Longrightarrow G_g+H_g$
$F_{1g}\otimes G_g$	12	$-\tau$	$\tau-1$	0	0	12	$-\tau$	$\tau-1$	0	0	$\Longrightarrow F_{2g}+G_g+H_g$
$F_{1g}\otimes H_g$	15	0	0	0	-1	15	0	0	0	-1	$\Longrightarrow F_{1g}+F_{2g}+G_g+H_g$
$F_{2g}\otimes F_{2g}$	9	$2-\tau$	$1+\tau$	0	1	9	$2-\tau$	$1+\tau$	0	1	$\Longrightarrow A_g+F_{2g}+H_g$
$F_{2g}\otimes G_g$	12	$\tau-1$	$-\tau$	0	0	12	$\tau-1$	$-\tau$	0	0	$\Longrightarrow F_{1g}+G_g+H_g$
$F_{2g}\otimes H_g$	15	0	0	0	-1	15	0	0	0	-1	$\Longrightarrow F_{1g}+F_{2g}+G_g+H_g$
$G_g\otimes G_g$	16	1	1	1	0	16	1	1	1	0	$\Longrightarrow A_g+F_{1g}+F_{2g}+G_g+H_g$
$G_g\otimes H_g$	20	0	0	-1	0	20	0	0	-1	0	$\Longrightarrow F_{1g}+F_{2g}+G_g+2H_g$
$H_g\otimes H_g$	25	0	0	1	1	25	0	0	1	1	$\Longrightarrow A_g+F_{1g}+F_{2g}+2G_g+2H_g$
$A_u\otimes A_u$	1	1	1	1	1	1	1	1	1	1	$\Longrightarrow A_g$
$A_u\otimes H_u$	5	0	0	-1	1	5	0	0	-1	1	$\Longrightarrow H_g$
$F_{1u}\otimes F_{1u}$	9	$1+\tau$	$2-\tau$	0	1	9	$1+\tau$	$2-\tau$	0	1	$\Longrightarrow A_g+F_{1g}+H_g$
$F_{1u}\otimes F_{2u}$	9	-1	-1	0	1	9	-1	-1	0	1	$\Longrightarrow G_g+H_g$
$F_{1u}\otimes G_u$	12	$-\tau$	$\tau-1$	0	0	12	$-\tau$	$\tau-1$	0	0	$\Longrightarrow F_{2g}+G_g+H_g$
$F_{1u}\otimes H_u$	15	0	0	0	-1	15	0	0	0	-1	$\Longrightarrow F_{1g}+F_{2g}+G_g+H_g$
$F_{2u}\otimes F_{2u}$	9	$2-\tau$	$1+\tau$	0	1	9	$2-\tau$	$1+\tau$	0	1	$\Longrightarrow A_g+F_{2g}+H_g$
$F_{2u}\otimes G_u$	12	$\tau-1$	$-\tau$	0	0	12	$\tau-1$	$-\tau$	0	0	$\Longrightarrow F_{1g}+G_g+H_g$
$F_{2u}\otimes H_u$	15	0	0	0	-1	15	0	0	0	-1	$\Longrightarrow F_{1g}+F_{2g}+G_g+H_g$
$G_u\otimes G_u$	16	1	1	1	0	16	1	1	1	0	$\Longrightarrow A_g+F_{1g}+F_{2g}+G_g+H_g$
$G_u\otimes H_u$	20	0	0	-1	0	20	0	0	-1	0	$\Longrightarrow F_{1g}+F_{2g}+G_g+2H_g$
$H_u\otimes H_u$	25	0	0	1	1	25	0	0	1	1	$\Longrightarrow A_g+F_{1g}+F_{2g}+2G_g+2H_g$

TABLE III. "Raman combination and overtones"—frequencies in cm^{-1}.

Frequency	Combination	Symmetry		
3148:	1574+1574,	A_g,H_g	contained	$[H_g]^{2}$[a]
2998:	1424+1574,	A_g,H_g	within	$H_g \otimes H_g$
2936:	1468+1468,	A_g		$[A_g]^2$
2846:	1424+1424,	A_g,H_g		$[H_g]^2$
2676:	1250+1424,	A_g,H_g		$H_g \otimes H_g$
2348:	772+1574,	A_g,H_g		$H_g \otimes H_g$
2330:	981+1346,	A_g,H_g		$F_{1g} \otimes F_{1g}$
2196:	1100+1100,	A_g,H_g		$H_g \otimes H_g$
2134:	710+1424,	A_g,H_g		$H_g \otimes H_g$
2014:	498+1521,	A_g,H_g		$G_g \otimes G_g$
1962:	496+1468,	A_g		$A_g \otimes A_g$
1838:	272+1574,	A_g,H_g		$H_g \otimes H_g$
1692:	272+1424,	A_g,H_g		$H_g \otimes H_g$

[a] $[\Gamma]^2$ represents the first-order overtone of Γ.

theory of higher-order absorption and scattering spectra can be applied to the case of elastic waves which propagate inside the crystal and whose behavior is subject to mutual interactions. But in the case of molecular crystals, perturbation methods can be applied. When an elastic wave deforms $C_{60}H_6$ or C_{60} molecules, the restoring forces of the intermolecular bonds are, in a first approximation, the same as those acting in the free molecules; on closer study, we must only add the coupling forces which link each ion to those which surround it. These forces are weak. Therefore, the equation for a fundamental frequency contains a principal term which is not dependent on the elastic wavelength and only a correction term which is. The dispersion of $\omega(\mathbf{q})$ is weak (5–10 cm^{-1} according to Ref. 20) and one can conceive that the overtone has a well-defined frequency.

To summarize, not only the fundamental vibration modes, but also sixteen additional weak Raman peaks of C_{60} have been observed in our experiment, which is similar to the reports of Denisov *et al.*[21] and Dong *et al.*[22] Three of them are attributed to silent modes due to the symmetry reduction and others are related to second-order Raman spectra of C_{60} on the basis of factor group analysis. These results indicate minor influences of the intermolecular coupling upon solidification of C_{60} on the high-frequency vibration of free molecules.

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