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Vibrational Raman Spectra of C_{70} and C_{70}^{6-} Studied by Density Functional Theory

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Vibrational frequencies of fullerene C_{70} and fulleride C_{70}^{6-} have been calculated with density functional theory at the B3LYP/6-31G* level. Raman activities are calculated using polarizability derivatives estimated by Hartree−Fock approximation. Good agreement with experiment is achieved when the calculated vibrational frequencies are uniformly scaled by a factor of 0.98 for C_{70}. Strong Raman peaks of C_{70} are assigned on the basis of both frequency and intensity information. Assignment for the weak Raman peaks is proposed. The calculated vibrational frequencies and intensities of C_{70}^{6-} are presented. The intensity changes of IR and Raman peaks on going from C_{70} to C_{70}^{6-} are also addressed.

Introduction

The vibrational Raman spectroscopy of fullerene C_{70} has attracted much attention since C_{70} was obtained in 1990.[1] Samples of mixtures of C_{60} and C_{70} were first used in the measurement, which led to tentative assignments of the strong peaks.[2] Dennis et al.[3] then reported the Fourier transform Raman spectrum of C_{70} from pure samples. Subsequent Raman scattering measurements were carried out on C_{70} samples in the form of thin films,[4−11] crystals,[12−15] and solutions.[14,15] Among these, several works used the depolarization ratio for peak assignment.[4,5,8,9] Raman excitation profiles (REP),[16,17] were also used to assign some of the fundamental peaks.

Theoretically, the vibrational frequencies of fullerene C_{70} have been subjected to many studies. The Raman spectrum of C_{70} was calculated by various theoretical methods including semiempirical methods,[15,18−22] force-field model,[9, 23−26] quantum consistent force field for π electrons (QCFF/PI),[27,28] tight-binding molecular dynamics (TB-MD),[29,30] Car-Parrinello molecular dynamics,[31] and local-density approximation (LDA)[32] within the density functional theory (DFT). Despite all these effort, a detailed band-by-band assignment of the Raman spectrum of C_{70} has yet to be achieved. This is partly due to the fact that all earlier calculated frequencies were not sufficiently accurate, given the large number of Raman-active modes (53) that exist within the 200−1600 cm^{-1} spectral range. The lack of calculated Raman intensities in many of the earlier calculations further hinders the comparison between theoretical and experimental results.

Research on C_{70}^{6-} has been focused on its electrochemical generation[33] and NMR properties.[34−36] Raman scattering measurement was performed on a thin film of C_{70} saturated with K, Rb, Cs.[10] Previous theoretical treatment of the Raman spectrum of C_{70}^{6-} was limited to a force-field model study.[25] Since large IR intensity enhancement has been reported [37] for C_{60}^{6-} and explained by the change in certain components of the atomic polar tensor,[38] it would be interesting to see whether C_{70}^{6-} follows the trend.

In this work, density functional theory is used to predict the harmonic vibrational frequencies for fullerene C_{70} and fulleride C_{70}^{6-}. When combined with a medium basis set, DFT at the B3LYP level gives good agreement with respect to experimental frequencies and intensities. This has also been illustrated in the case of the IR spectrum of fullerenes C_{60} [39] and C_{70}.[40] The intensity of Raman peaks is estimated from polarizability derivatives calculated at the Hartree−Fock (HF) level. A new assignment of the Raman spectrum of C_{70} is proposed based on both the frequency and intensity of the fundamental modes. The intensities of IR and Raman peaks of C_{70}^{6-} are compared with that of C_{70}.

Computational Method

The geometries and vibrational frequencies of C_{70} and C_{70}^{6-} are calculated using density functional theory. The hexa-charged species C_{70}^{6-} is studied because the doubly degenerate LUMO and the nondegenerate LUMO + 1 of C_{70} are very close in energy, being separated by less than 0.1 eV. Becke's three-parameter (B3) hybrid functional[41] with exact exchange in combination with Lee, Yang, and Parr's (LYP) gradient-corrected correlation functional[42] is used. An additional calculation is performed with the HF approximation using the B3LYP optimized geometry to get the polarizability derivatives, from which the Raman activities are calculated. The common practice to scale the theoretical vibrational frequencies is used to improve the agreement between theoretical and experimental results. Since a uniform scaling factor of 0.98 gives satisfactory agreement for vibrational frequencies,[40] it is used in this study. Isotope effect on C_{70} and C_{70}^{6-} is examined by vibrational analysis where one of the seventy carbon atoms is changed to ^{13}C. All five possible sites of substitution are investigated. The standard double-ζ quality basis set 6-31G* is used throughout this work. All calculations are carried out with Gaussian98 program[43] on an SGI Origin200 server with four R10000/180 MHz CPUs.

Results and Discussion

Structures of C_{70} and C_{70}^{6-}. The calculated bond lengths for C_{70} and C_{70}^{6-} are listed in Table 1. The overall dimensions of the cage, measured as the distance between the corresponding carbon atoms in the five-membered rings in the two caps (d_a) and the distance between the two farthest separated atoms on the equator (d_b), are also listed. C_{70} has eight unique bonds as shown in Figure 1. In the cap area, bonds 1, 3, and 5 are within

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TABLE 1: Bond Lengths and Dimensions of C_{70} and $C_{70}{}^{6-}$ Calculated by B3LYP/6-31G*

bond[a]	C_{70}[b]	$C_{70}{}^{6-}$
1	1.452	1.451
2	1.397	1.435
3	1.448	1.446
4	1.389	1.428
5	1.449	1.439
6	1.434	1.475
7	1.421	1.431
8	1.471	1.485
d_a	7.940	7.987
d_b	7.087	7.118

[a] See Figure 1 for bond numbering; bond lengths are in Å. [b] Identical results for bond lengths of C_{70} were reported in ref 40.

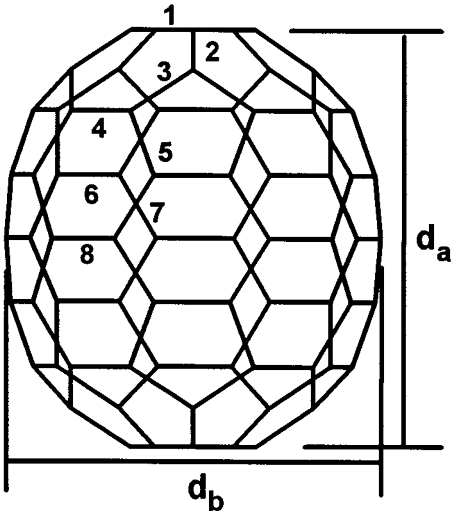

Figure 1. Fullerene C_{70}, as looking down a C_2 rotation axis. Bonds are numbered in order from cap to equator.

five-membered rings and their lengths are between 1.448 and 1.452 Å, corresponding to the long bond in C_{60}. Bonds 2 and 4, predicted as 1.397 and 1.389 Å, respectively, connect two five-membered rings and are much shorter, corresponding to the short bond in C_{60}. These data are consistent with the theoretical values of C_{60} calculated at the save level of theory,[38] as well as experimental results.[44,45] Near the equator, bond 6 lies within a five-membered ring, but is shorter than bonds 1, 3, and 5 by about 0.015 Å. Bond 7 extends from a five-membered ring to a six-membered ring. All rings around bond 8, the longest bond in C_{70}, are six-membered. Identical results have been reported earlier by Stratmann et al.[40] where good agreement with experiment was obtained.

The six extra electrons of $C_{70}{}^{6-}$ have different effects on different bonds. The long bonds 1, 3, and 5 in the cap regions are slightly shortened from C_{70} to $C_{70}{}^{6-}$, whereas both short bonds 2 and 4 are significantly elongated by about 0.04 Å. These changes are in agreement with the structural change in $C_{60}{}^{6-}$ with respect to C_{60} as predicted by same level of theory.[38] In the equator region, bond 6 is elongated by 0.04 Å, and bonds 7 and 8 by about 0.01 Å. The overall length of the molecule increases by 0.05 Å and the diameter increases by 0.03 Å as a result of the negative charge. A similar trend was observed for the diameters of C_{60} and $C_{60}{}^{6-}$ at the same level of theory.[38]

Raman Spectrum of C_{70}. Fullerene C_{70} has D_{5h} point group symmetry. From the 204 vibrational modes of C_{70}, 122 unique frequencies ($12A_1'$(Raman) + $9A_2'$ + $21E_1'$(IR) + $22E_2'$(Raman) + $9A_1''$ + $10A_2''$(IR) + $19E_1''$ (Raman) + $20E_2''$) result. Of the 122 unique frequencies, 31 are IR active and 53 are Raman active. The rest are silent modes. Table 2 lists the 122 calculated frequencies of C_{70} according to their symmetry. We will concentrate on the Raman spectrum of fullerene C_{70}, since other authors [40] have addressed the IR spectrum at this level of theory earlier and found satisfactory agreement with experiment.

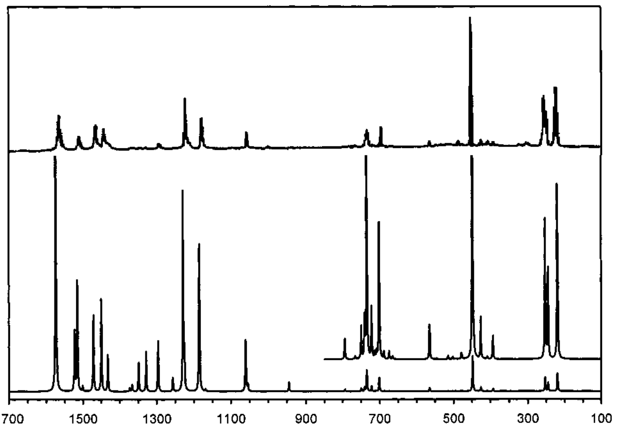

Figure 2. Simulated Raman spectrum (bottom) of fullerene C_{70} predicted by DFT at the B3LYP/6-31G* level is shown. Experimental spectrum (top, taken from ref 14) is shown for comparison.

Table 3 compares the predicted frequencies and intensities of Raman active modes with those from selected experiments.[4,8,10,14,17] Six frequencies with relatively low intensities are predicted to be within 2 cm^{-1} to peaks with high intensities. These peaks will probably be invisible in experiment. Simulated Raman spectrum is also shown in Figure 2 alongside the experimental result.

Relative intensities from Fourier transform Raman measurement for crystalline C_{70} have been reported by Lynch et al.[14] and will be used to compare with our data. Among the more than 70 reported experimental peaks, fourteen peaks at 226, 251, 259, 455, 701, 736, 1060, 1182, 1221, 1227, 1445, 1467, 1511, and 1564 cm^{-1} have relative intensities larger than 10% of the highest peak. We will refer these peaks as strong peaks since they are present in most of the experimental spectra in the literature. They are shown in bold in Table 3. In our predicted spectrum, vibrational modes with large intensities are found at positions very close to these experimental frequencies. This allows us to assign them with confidence. When compared with earlier theoretical assignments for the strong peaks, we found more agreement with Brockner and Menzel[15] than with the others.

To date, the most extensive experimental assignment of Raman spectrum for C_{70} is based on the Raman excitation profiles[17] where 24 peaks were assigned. When compared with our result, most of the reported A_1' modes are in agreement with ours, whereas discrepancy exists for more than half of the E_1'' and E_2' modes. Other experimental assignments[5,9] of the strong peaks, based on depolarization ratio measurement, have more discrepancies.

Besides the fourteen strong peaks, more than sixty reported peaks have relative intensities between 4 and 10%.[14] Because of their low intensities, none of these peaks can be unambiguously classified as fundamental mode. After the strong peaks are assigned, we try to assign the weak peaks by considering both the calculated frequency and intensity. Below, we divide the whole spectrum (200−1600 cm^{-1}) into five regions and discuss each region in turn.

In the 200−700 cm^{-1} range, seventeen fundamental frequencies are predicted. In the experiment,[14] four strong peaks are

TABLE 2: Theoretical Vibrational Frequencies of All Fundamental Modes for C_{70} Calculated by Density Functional Theory[a]

IR				Raman						Silent		
A_2''		E_1'		A_1'		E_2'		E_1''		A_2'	A_1''	E_2''
318.0	0.2	325.7	0.1	253.3	46.9	219.6	62.7	245.3	30.2	485.2	336.3	304.4
458.8	11.2	358.2	0.6	393.4	7.8	298.9	0.1	408.3	0.8	545.8	529.3	382.6
563.9	11.7	414.5	0.3	448.3	120.6	426.1	13.1	478.6	2.1	628.8	612.0	406.9
703.8	0.0	507.2	0.2	564.7	12.4	502.4	0.9	514.9	1.2	732.3	733.6	514.7
895.8	0.5	533.1	34.5	701.4	48.9	533.5	0.0	546.0	0.3	744.6	779.3	555.4
1142.9	14.2	573.1	24.9	708.8	2.3	665.2	1.1	674.5	3.1	935.9	891.8	632.9
1205.6	1.7	639.5	13.1	1060.9	156.8	688.5	2.6	713.5	2.4	1215.1	1240.4	700.5
1320.8	2.2	665.5	22.1	1185.1	440.6	722.1	16.2	734.7	65.1	1338.2	1347.3	717.1
1462.4	8.9	729.3	0.0	1229.0	618.1	734.7	6.5	740.2	4.3	1450.0	1557.8	727.6
1567.6	0.8	751.3	18.1	1449.7	309.8	741.1	10.1	794.3	7.0			781.3
		827.7	0.0	1471.5	271.6	750.2	10.5	1054.4	25.7			920.0
		905.0	0.3	1574.0	806.4	766.5	1.0	1168.7	6.9			1074.5
		1087.2	4.0			945.0	29.5	1225.5	118.3			1155.6
		1176.9	0.6			1059.0	24.8	1296.3	170.6			1257.6
		1254.6	1.3			1186.7	82.1	1312.8	0.1			1315.7
		1290.3	2.5			1256.9	44.0	1366.2	21.5			1327.3
		1318.2	1.8			1328.9	126.3	1432.1	114.9			1398.5
		1415.1	15.8			1349.1	91.2	1515.5	427.9			1454.7
		1431.1	198.9			1372.9	11.4	1573.7	354.3			1516.5
		1489.1	8.4			1501.0	15.6					1572.7
		1569.2	3.9			1523.0	186.2					
						1573.2	14.8					

[a] Harmonic frequencies (in cm^{-1}) are calculated at the B3LYP/6-31G* level and scaled by 0.98. IR intensities are in km/mol and Raman activities in $Å^4$/amu.

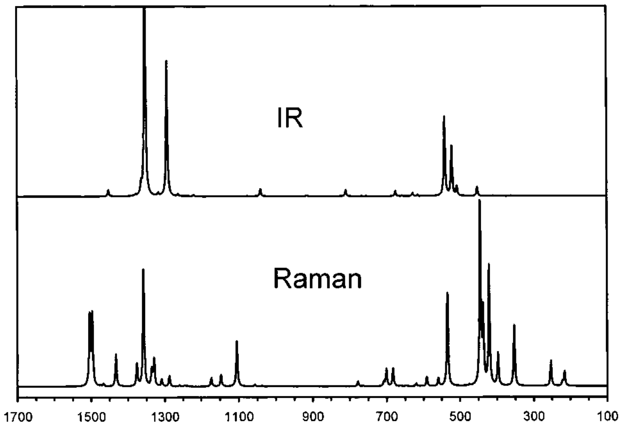

Figure 3. Simulated IR and Raman spectra of fulleride $C_{70}{}^{6-}$ predicted by DFT at the B3LYP/6-31G* level.

observed at 226, 251, 259 and 455 cm^{-1}. Our calculation predicts four peaks at 219.6(E_2'), 245.3(E_1''), 253.3(A_1'), and 448.3(A_1') cm^{-1} having intensities significantly larger than other peaks. These strong peaks are assigned to the experimental peaks. Earlier assignments for these strong peaks based on theory by Brockner and Menzel[15] and experiment by Gallagher et al.[17] are in agreement with ours. For the rest of the thirteen fundamental vibrational modes, there are 22 candidates in the experiment. We assign them to the experimental peaks with the closest frequency.

In the 700−1000 cm^{-1} range twelve fundamental frequencies are calculated. Two strong experimental peaks[14] occurring at 701 and 736 cm^{-1} are well reproduced by our result and are assigned to 701.4(A_1') and 734.7(E_1'') cm^{-1}, respectively. Four other fundamentals with medium or low intensity are predicted between these two strong peaks and are assigned to experimental peaks with the closest frequencies. Between 750 and 800 cm^{-1}, most experiments show a medium peak at 768 cm^{-1}. There are two E_2' candidates (741.1 and 750.2 cm^{-1}) with noticeable intensity in our calculation, but both frequencies are lower than the observed peak. In the earlier study[40] on the IR spectrum of C_{70}, the peaks in this region were underestimated by up to 44 cm^{-1} at the same level of theory. With that in mind, we assign the 768 cm^{-1} peak to the predicted 750.2 cm^{-1}. The rest of this region (800−1000 cm^{-1}) has only one calculated peak at 945.0 cm^{-1} with medium intensity, which is in good agreement with experimental value of 946 cm^{-1}.

In the 1000−1400 cm^{-1} range, fifteen peaks are predicted. Four strong Raman peaks occur at 1060, 1182, 1221, and 1227 cm^{-1} in the Lynch experiment.[14] These peaks are assigned to A_1', A_1', E_1'', and A_1', respectively, according to the calculated frequency and intensity. This assignment agrees with earlier attempts based on theory.[15] The rest of the eleven weak fundamental peaks are assigned to experimental peaks having the closest frequency.

In the 1400−1600 cm^{-1} range, nine fundamental frequencies are predicted. Four strong peaks are observed[14] at 1445, 1467, 1511, and 1564 cm^{-1} and are assigned mainly to the A_1', A_1', E_1'', and A_1' modes, respectively. Three fundamental modes are predicted to lie within 1 cm^{-1} of 1574 cm^{-1} and two of them, E_1'' and A_1', have significant intensities. Thus the 1564 cm^{-1} is assigned to gain intensity from these fundamentals, with the A_1' mode having the largest contribution. The observed peak at 1511 cm^{-1} probably has intensity contribution from the E_2' mode calculated at 1523 cm^{-1}, in addition to the E_1'' mode calculated at 1515.5 cm^{-1}. Earlier assignment based on theory[15] is in agreement with ours for the first two strong peaks, whereas only one fundamental is assigned to each of the latter two. The other two peaks in this region are weak and are assigned to experimental peaks at 1430 and 1494 cm^{-1}.

Several experiments show a weak Raman peak at 1458 cm^{-1}. However, in our calculated spectrum two strong A_1' peaks at 1449.7 and 1471.4 cm^{-1} are assigned to 1446 and 1467 cm^{-1}, respectively. Between these two strong peaks, there is no other fundamental peak. We performed frequency calculations on systems where one carbon atom is substituted by ^{13}C. The results show that the only Raman peak that is significantly affected is the 1515.5(E_1'') cm^{-1}, which is lowered by 6 cm^{-1}. Thus, the isotope effect cannot explain the observed 1458 cm^{-1} peak. Overtone ($2 \times 736 = 1472$ cm^{-1}) and combination frequencies ($251 + 1221 = 1472$ cm^{-1}) are two possible explanations. Other authors[15] attributed the 1458 cm^{-1} peak to an IR mode, which

TABLE 3: Assignment of Experimental Raman Frequencies of Fullerene C_{70}[a]

sym.	frequency	activity [b]	Lynch [c]	Wang [d]	Bethune [e]	Gallagher[f]	Chandrabhas [g]
E_2'	219.6	62.6	**226**	228		233	
E_1''	245.3	30.2	**251**			250	250.1
A_1'	253.3	46.9	**259**	258	261	257	257.2
E_2'	298.9	0.1	302				
A_1'	393.3	7.8	396	399	400	396	
E_1''	408.3	0.8	410	409	411	410	409.4
E_2'	426.1	13.1	430				428.2
A_1'	448.3	120.6	**455**	455	459	452	455.0
E_1''	478.6	2.1	480				494.3
E_2'	502.5	0.9	506	508	501	506	505.6
E_1''	514.8	1.2	511				
E_2'	533.5	0.03	536				
E_1''	545.9	0.3	549				
A_1'	564.6	12.4	568	569	573	569	576.3
E_2'	665.3	1.1	668				
E_1''	674.5	3.1	676				
E_2'	688.6	2.6	690				
A_1'	701.4	48.9	**701**	701	704	701	701.6
A_1'	708.8	2.3					710.0
E_1''	713.6	2.4	713	714		714	
E_2'	722.1	16.2	721				
E_1''	734.7	65.1	**736**	737	739	738	737.5
E_2'	734.7	6.5	(736)				
E_1''	740.2	4.3	(762)				
E_2'	741.1	10.1	762				
E_2'	750.2	10.5	768	766	770	769	768.1
E_2'	766.5	1.0	786				
E_1''	794.3	7.0	801				
E_2'	945.0	29.5	946				
E_1''	1054.4	25.7					
E_2'	1059.0	24.8	(1060)				
A_1'	1060.9	156.8	**1060**	1062	1062	1060	1061.4
E_1''	1168.7	6.9	1163	1165			
A_1'	1185.1	440.6	**1182**	1182	1186		1184.0
E_2'	1186.7	82.1	(1182)				
E_1''	1225.5	118.3	**1221**				1217.2
A_1'	1229.0	618.1	**1227**	1227	1231	1227	1229.5
E_2'	1256.8	44.0	1257	1257	1260	1256	1258.2
E_1''	1296.3	170.6	1296	1296	1298	1296	
E_1''	1312.8	0.1		1313	1317	1311	
E_2'	1328.9	126.3	1331	1335	1336	1333	1335.0
E_2'	1349.1	91.2	1349				
E_1''	1366.2	21.5	1366	1367	1370	1366	1369.2
E_2'	1372.9	11.4	1374				
E_1''	1432.1	114.9	1430				1437.5
A_1'	1449.7	309.8	**1445**	1447	1448	1446	1447.7
A_1'	1471.4	271.6	**1467**	1469	1471	1468	1469.3
E_2'	1501.0	15.6	1494	1493			
E_1''	1515.5	427.9	**1511**	1515	1517	1512	1516.9
E_2'	1523.0	186.2	(1511)				
E_2'	1573.2	14.8	(1564)				
E_1''	1573.7	354.3	(1564)				
A_1'	1574.0	806.4	**1564**	1565	1569	1566	1565.9

[a] Frequencies (cm^{-1}) are calculated at the B3LYP/6-31G* level and scaled by 0.98. [b] Raman activity (Å^4/amu) is calculated from polarizability derivatives estimated by HF. [c] Taken from ref 14. Strong peaks (in bold) have relative intensities larger than 10% of the highest peak. [d] Taken from ref 10. [e] Taken from ref 4. [f] Taken from ref 17. [g] Taken from ref 8.

also appears reasonable since there is a weak IR mode at 1462.4 cm^{-1} in our result.

Overall, the predicted frequencies and intensities for all strong Raman peaks of C_{70} are in good agreement with the experimental result.

Vibrational Spectra of C_{70}^{6-}. The calculated vibrational frequencies and the intensities of the IR and Raman active modes of fulleride C_{70}^{6-} are listed in Table 4. Simulated IR and Raman spectra are shown in Figure 3. The predicted spectral range of C_{70}^{6-} is 216−1504 cm^{-1}, shrinking by almost 70 cm^{-1} from 220 to 1574 cm^{-1} for C_{70}. Most of the frequencies are downshifted by various amounts. However, four peaks at 915.2(A_2''), 1218.1(A_2''), 1259.1(A_1'), and 1351.8(A_2'') cm^{-1} are increased by more than 5 cm^{-1}.

One experimental study[10] has addressed the Raman spectrum of C_{70}^{6-} where C_{70} film was saturated with alkali metals, M = K, Rb, or Cs to give nominal configuration of M_6C_{70}. Similar spectra were obtained from different dopants and only strong peaks were reported. When compared with our predicted frequencies, moderate agreement can be seen for Raman peaks below 1000 cm^{-1}. For peaks above that, large differences are seen. Indeed, the highest peak in the experiment compares better with the un-scaled frequency (1534.5 cm^{-1}) than with the scaled frequency (1503.8 cm^{-1}). Poor agreement with the theoretical result and low resolution of the experimental spectra make further measurements necessary.

IR and Raman Intensities of C_{70} and C_{70}^{6-}. When C_{70} receives six electrons to become C_{70}^{6-}, the intensities of seven

TABLE 4: Theoretical Vibrational Frequencies of All Fundamental Modes for C_{70}^{6-} Calculated by Density Functional Theory[a]

IR				Raman						Silent		
A_2''		E_1'		A_1'		E_2'		E_1''		A_2'	A_1''	E_2''
321.0	0.2	304.5	0.5	253.0	93.1	215.8	54.1	222.3	16.2	447.5	297.6	278.9
409.2	1.8	361.1	1.5	397.5	119.8	290.2	0.1	353.5	223.3	533.8	413.6	297.0
540.0	293.4	400.0	0.0	437.1	262.9	412.3	0.4	420.7	439.4	595.2	588.9	358.9
625.6	1.0	452.0	33.5	533.9	342.2	474.9	3.7	444.7	666.7	668.9	591.8	440.5
915.2	1.7	507.2	34.3	644.8	2.1	519.7	1.4	499.0	0.0	733.2	759.8	541.5
1075.7	0.9	520.8	184.1	683.0	65.7	591.4	34.3	559.5	28.7	918.4	874.7	544.4
1218.1	5.4	614.9	5.4	1059.1	2.6	614.2	1.4	620.3	10.7	1203.1	1200.5	599.1
1292.0	500.6	628.1	11.8	1114.5	1.7	649.2	1.7	662.2	1.4	1333.0	1270.0	622.4
1351.8	1016.2	657.1	2.3	1259.1	4.7	661.2	0.9	701.3	63.9	1432.6	1455.5	631.1
1452.1	23.5	674.6	19.1	1358.0	430.7	677.7	2.4	778.1	18.7			770.2
		809.0	22.7	1375.5	82.3	708.1	16.5	1037.9	3.5			904.1
		872.0	0.1	1503.8	254.7	763.2	2.3	1104.8	165.9			1026.4
		1040.5	27.7			905.0	0.0	1173.1	32.0			1129.9
		1165.6	0.1			1056.1	5.4	1238.1	3.2			1179.6
		1233.9	2.1			1147.5	42.1	1286.6	34.3			1222.7
		1261.0	8.7			1245.3	4.5	1308.0	26.3			1291.4
		1315.8	10.7			1287.6	5.2	1335.9	50.0			1333.8
		1362.5	35.5			1329.0	98.0	1432.9	118.2			1398.4
		1379.2	3.7			1334.3	23.8	1475.1	3.5			1422.6
		1441.1	1.4			1418.1	1.9					1454.1
		1504.1	0.1			1466.7	8.9					
						1497.1	258.1					

[a] Harmonic frequencies (in cm^{-1}) are calculated at the B3LYP/6-31G* level and scaled by 0.98. IR intensities are in km/mol and Raman activities in Å^4/amu.

TABLE 5: Intensity Change in IR and Raman Spectra of C_{70} and C_{70}^{6-} [a]

	C_{70}		C_{70}^{6-}		
IR	freq	int	Freq	int	C_{70}^{6-}/C_{70}
E1′	507.2	0.2	452.0	33.5	167.50
A2″	563.9	11.7	540.0	293.4	25.08
E1′	827.7	0.0	809.0	22.7	1080.95
A2″	1320.8	2.2	1351.8	1016.2	461.91
E1′	1431.1	198.9	1379.2	3.7	0.02
A2″	1462.4	8.9	1292.0	500.6	56.25
A2″	1567.6	0.8	1452.1	23.5	29.38

	C_{70}		C_{70}^{6-}		
Raman	freq	int	Freq	int	C_{70}^{6-}/C_{70}
A1′	393.4	7.8	397.5	119.8	15.36
E1″	408.3	0.8	353.5	223.3	279.13
E1″	478.6	2.1	420.7	439.4	209.24
E1″	546.0	0.3	444.7	666.7	2222.33
A1′	564.7	12.4	533.9	342.2	27.60
E2′	688.5	2.6	591.4	34.3	13.19
E2′	945.0	29.5	905.0	0.009	0.00
A1′	1060.9	156.8	1059.1	2.6	0.02
E1″	1168.7	6.9	1104.8	165.9	24.04
A1′	1185.1	440.6	1114.5	1.7	0.00
A1′	1229.0	618.1	1259.1	4.7	0.01
E2′	1256.9	44	1245.3	4.5	0.10
E1″	1296.3	170.6	1238.1	3.2	0.02
E1″	1312.8	0.1	1308.0	26.3	263.00
E2′	1328.9	126.3	1287.6	5.2	0.04
E1″	1515.5	427.9	1475.1	3.5	0.01
E2′	1523.0	186.2	1466.7	8.9	0.05
E2′	1573.2	14.8	1497.1	258.1	17.44

[a] Peaks (cm^{-1}) of C_{70} and C_{70}^{6-} corresponding to same vibrational mode whose intensity increases or decreases by a factor of 10 or more. IR intensities are in km/mol and Raman activities in Å^4/amu.

IR peaks and eighteen Raman peaks are predicted to increase or decrease by a factor of 10 or more. Table 5 lists these peaks. The intensities of six of the seven IR peaks increase. Significant intensity gains are seen for peak at 540.0, 1292.0 and 1351.8 cm^{-1} for C_{70}^{6-}, which indeed are the three strongest IR peaks of C_{70}^{6-}. On the other hand, the strongest peak of C_{70} at 1431.1 cm^{-1} diminishes.

For the Raman spectrum, intensity enhancement is mainly seen in the range of 200−600 cm^{-1}. In the 600−1600 cm^{-1} region, most peaks decrease in intensity.

Conclusion

Vibrational frequencies of fullerene C_{70} and fulleride C_{70}^{6-} have been calculated by the density functional theory at the B3LYP/6-31G* level. The intensity of the Raman active modes are estimated on the basis of the polarizability derivatives calculated by HF approximation. The strong Raman peaks are well reproduced in our calculation for both the frequency and the intensity, which leads to assignment of the experimental peaks. The assignment of the weak Raman peaks is proposed. The intensity enhancement seen for C_{60}^{6-} is predicted for the IR spectrum of C_{70}^{6-}. For the Raman spectrum of C_{70}^{6-}, intensity enhancement is predicted for peaks below 600 cm^{-1}, whereas the most intensity changes are reduction for peaks above 600 cm^{-1}. A full assignment of the vibrational frequencies of C_{70}^{6-} awaits future experiments.

Note Added in Proof

A recent paper[46] reported calculated Raman frequencies of C_{70} using the same level of theory. The reported assignments of the experimental Raman peaks are similar but not identical to those given here.

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