Infrared and Raman Spectroscopy of 9,9′-Spirobifluorene, Bis(2,2′-biphenylene)silane, and Bis(2,2′-biphenylene)germane. Vibrational Assignment by Depolarization Measurement and HF and Density Functional Theory Studies

Bong Hyun Boo,*,† Jaiwook Park,‡ Hwan Gon Yeo,§ Sang Yeon Lee,|| Chan Jo Park,† and Jin Ho Kim†

Department of Chemistry, Chungnam National University, Taejon 305-764, Korea, Center for Molecular Science, 373-1 Kusung-dong, Yusung-gu, Taejon 305-701, Korea, Department of Chemistry, Pohang University of Science and Technology, Pohang 790-784, Korea, Agency for Defence Development, Taejon 305-600, Korea, and Department of Industrial Chemistry, Kyungpook National University, Taegu 702-701, Korea

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The infrared and Raman spectra of 9,9′-spirobifluorene (SBFL), bis(2,2′-biphenylene)silane (BBPS), and bis-(2,2′-biphenylene)germane (BBPG) are measured, and the vibrational frequencies and modes for these molecules are assigned by ab initio Hartree−Fock and Becke 3-Lee−Yang−Parr (B3LYP) density functional theory (DFT) calculations using the 4-31G and 3-21G basis sets for SBFL and for BBPS and BBPG, respectively. Assignment of some of the vibrational modes of SBFL is also confirmed by solution Raman spectroscopy with the depolarization method. Comparison of the calculated and experimental vibrational spectra reveals that the DFT calculations are quite accurate in predicting the vibrational frequencies, intensities, and modes. It is found that the central Si and Ge atoms dominantly enhance some of the IR intensities of the vibrations involving only the M−C_4 (M = Si, Ge) antisymmetric stretching motion. The enhancement of some of the infrared intensities is accounted for by the increase of the electric dipole moment involving the M−C_4 vibrations due to the presence of the small electronegative Si and Ge atoms in the central position.

Introduction

Spiro compounds consist of two mutually perpendicular π-systems connected via a common insulating tetracoordinate atom. The structural characteristics of spiro compounds have been theoretically[1−7] and experimentally[8−12] studied. Previous theoretical calculation indicates that the overlap integral of two p_π orbitals in the different plane of spiro[4.4]nonatetraene is about 20% of the adjacent p orbitals in planar π electron systems.[1]

The electronic−vibrational spectra of 9,9′-spirobifluorene (SBFL) are the subject of ongoing spectroscopic investigations. Recently, a van der Waals complex of SBFL with Ar, N_2 and H_2O was studied with laser-induced fluorescence spectroscopy in the free jet expansion to observe one origin transition of the bare molecule at 33 039 cm^{-1} and variation of the spectral shifts with cluster size.[10] The electronic and vibrational bands in the S_1 excited state were analyzed.[11,12]

Published results show that the vibrational frequencies appended to the 0_0^0 band origin of SBFL consist of fundamentals, overtones, and combination bands.[10−12] Thus correct assignment of the ground-state fundamentals is necessary to elucidate the electronic−vibrational spectra.

Computational methods based on density functional theory (DFT) are becoming widely used. These methods predict relatively accurate molecular structures and vibrations with moderate computational effort. Published results indicate that DFT methods reproduce experimental fundamentals with higher accuracy than do the HF and MP2 calculations.[13−23] Even when a uniform scaling factor is applied to the computed vibrational frequencies, DFT methods give better agreement with the experimental frequencies than do the HF and MP2 methods.[13,15−17,23] Some examples of the calculation on the vibrational frequencies of benzene are represented by Handy et al.[15,16] and Wheeless et al.,[18] in which MP2 calculations obtained by using 6-311G(d,p) basis set still underestimate the vibrational frequencies corresponding to the ring torsion and overestimate the vibrational frequency corresponding to a b_{2u} mode, which tends to dissociate into three acetylene molecules. On the other hand, these frequencies are accurately predicted by the DFT calculation using the Becke−Lee−Yang−Parr (BLYP) functional.[15,16,18]

Rauhut and Pulay employed BLYP and B3LYP functional methods using the 6-31G* basis set to predict fundamentals of 20 small molecules such as benzene, ether, and methanol, of which vibrational frequencies are exactly assigned. Meanwhile, they derived uniform scaling factors of 0.995 and 0.963 for BLYP and B3LYP, respectively, having root-mean-square (rms) deviations of 26.2 and 18.5 cm^{-1}, respectively.[19] When these workers applied these scaling factors to another 11 molecules such as aniline, ethanol, and oxetane, the rms deviations turned out to be 26.9 and 19.7 cm^{-1} for the BLYP and B3LYP methods, respectively, not very different from those of the molecules mentioned above.

We have measured the infrared and Raman spectra of 9,9′-spirobifluorene (SBFL) and its Si and Ge analogues of bis(2,2′-biphenylene)silane (BBPS) and bis(2,2′-biphenylene)germane (BBPG) and performed the normal vibrational mode analyses at the HF and B3LYP levels of theory using the 4-31G basis

† Chungnam National University and Center for Molecular Science.
‡ Pohang University of Science and Technology.
§ Agency for Defense Development.
|| Kyungpook National University.

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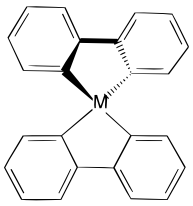
set for SBFL and a relatively smaller basis set for BBPS and BBPG such as 3-21G to examine whether the DFT method could



M = C
9,9′-Spirobifluorene,

M = Si
Bis(2,2′-biphenylene)silane,

M = Ge
Bis(2,2′-biphenylene)germane

reproduce correctly or not the vibrational frequencies and intensities of the Si- and Ge-containing molecules and to elucidate how the central Si and Ge atoms affect the peak positions and intensities in the infrared and Raman spectra.

We have assigned the fundamentals of the molecules by comparing the experimental peak positions and peak intensities with the theoretical ones. It is shown in this study that the B3LYP calculation, even when the relatively small basis set such as 3-21G is used, could reliably reproduce the experimental vibrational frequencies. It is also found that the central Si and Ge atoms dominantly enhance some of the IR intensities of the vibrations involving only the $M-C_4$ antisymmetric stretching motion.

Experimental and Theoretical Methods

Synthesis of 9,9′-spirobifluorene. The compound was synthesized by the Clarkson and Gomberg method.[24] The mp of SBFL was 199−201 °C (not corrected) (198−199 °C[24]). The purity was checked by TLC and ^{1}H NMR and mass spectroscopy. ^{1}H NMR (80 MHz) ($CDCl_3$): δ 7.84 (d, 4H, J = 7.4 Hz), 7.32 (dd, 4H, J = 7.3 Hz, 7.4 Hz), 7.09 (dd, 4H, J = 7.4 Hz, 7.3 Hz), 6.71 (d, 4H, J = 7.4 Hz). MS (70 eV) *m/z* (relative intensity): $(M + 1)^+$ 317 (47), M^+ 316 (100), 315 (80), 289 (11), 157 (20).

Synthesis of 2,2-Dilithiobiphenyl (DLBP). The compound was synthesized by the Gilman and Gorsich method.[25] To a solution of biphenyl (2.52 g, 16.3 mmol) and tetramethylethylenediamine (TMEDA) (5.80 mL, 38.4 mmol) in hexane (100 mL) was added *n*-buthyllithium (*n*-BuLi) (1.6 M in hexane, 24.6 mL, 39 mmol) dropwise at room temperature. The reaction mixture was stirred at 60 °C for 2 h to obtain yellowish red microcrystals of the complex of DLBP and TMEDA. The crystals were washed with hexane and were dried in vacuo to obtain 2.3 g in 50% yield.

Synthesis of Bis(2,2′-biphenylene)silane. This compound was synthesized by the Gilman and Gorsich method.[26] To a solution of tetrachlorosilane ($SiCl_4$) (0.43 mL, 3.8 mmol) in ether (10 mL) at −78 °C was added , a solution of the complex of DLBP and TMEDA (2.12 g, 7.51 mmol) in ether (20 mL) dropwise through a canula. The reaction mixture was heated to reflux for 2 h. Subsequently, 10 mL of benzene was added, and the mixture was refluxed for 2 h. After quenching with water the organic layer was separated, dried over anhydrous $MgSO_4$, and filtered. The solid obtained by removal of solvent from the filtrate was recrystallized from hexane to give white crystals of BBPS of 1.25 g in a quantitative yield.

Synthesis of Bis(2,2′-biphenylene)germane (BBPG). This compound was synthesized by the Gilman and Gorsich method.[26] Tetrachlorogermane ($GeCl_4$) (0.23 mL, 2.0 mmol) and the complex of DLBP and TMEDA (2.12 g, 7.51 mmol) were allowed to react as described in the preceding experiment for the preparation of BBPS to give 0.20 g of BBPG in 27% yield.

A Spectra-Physics 2060-7S Beam Lok Ar ion laser at the wavelength of 514.5 nm was used for the sample excitation.

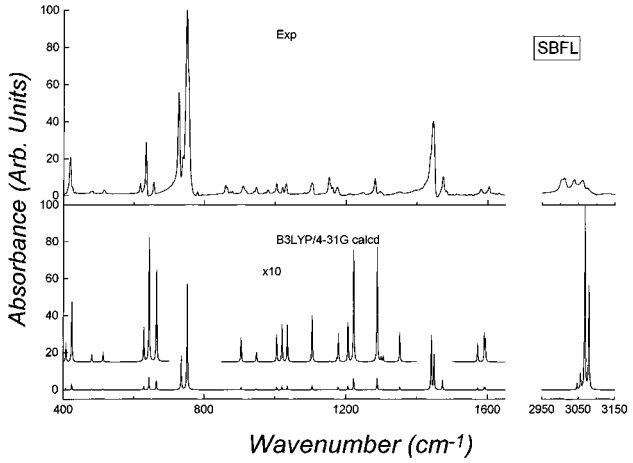


Figure 1. Comparison of the experimental (upper) and calculated (lower) infrared spectra of 9,9′-spirobifluorene.

The scattered light was collected through a collecting lens and focused on the slit of a Jobin-Yvon U-1000 double monochromator with a focal length of 1 m. The monochromatized photon was detected by a Hamamatsu R943-02 photomultiplier tube which can be cooled to −20 °C. The crystal was mounted on the specimen holder of a microscope with magnification set to 500. The magnification of 500 was chosen out of three available magnifications, 100, 500, and 1000, because it gave us the best views of the crystal to irradiate the laser to the fine surfaces of the crystal. Raman spectra of SBFL dissolved in carbon tetrachloride were obtained by replacing the microscope with a solution sample chamber. Saturated CCl_4 solution was used to obtain Raman bands as strong as possible. The depolarization ratio in the solution was obtained by dividing the count rate of the scattered light of which the electric vector is perpendicular to the electric vector of the incident light by the parallel count rate. The spectral resolution was 0.15 cm^{-1} at the slit width of 10 μm. The IR spectra of the KBr pellet were measured by a Digilab-FTS-80 FTIR spectrometer. The spectral resolution was 2 cm^{-1}.

The molecular geometries were optimized at the HF and B3LYP levels of theory with basis sets of 4-31G for SBFL and 3-21G for BBPS and BBPG by using the Gaussian 94 program[27] at SERI in Korea. Vibrational frequencies were computed with the HF/4-31G (SBFL), B3LYP/4-31G (SBFL), HF/3-21G (BBPS and BBPG), and B3LYP/3-21G (BBPS and BBPG), and they were uniformly scaled by 0.893 (HF/4-31G for SBFL), 0.958 (B3LYP/4-31G for SBFL), 0.904 (HF/3-21G for BBPS), 0.973 (B3LYP/3-21G for BBPS), 0.900 (HF/3-21G for BBPG), and 0.968 (B3LYP/3-21G for BBPG). The frequencies and normal modes were determined by diagonalizing the mass-weighted force constant matrix.

Results and Discussion

We have performed a variety of normal vibrational mode analyses of SBFL, BBPS, and BBPG. In Figures 1−6, we present a comparison of the experimental and DFT theoretical infrared and Raman spectra in the range except $1650 < \nu < 2900$ cm^{-1}, in which other peaks except the overtone bands are not observed. It is noticed that the simulated spectra have a Lorentzian distribution, having a fwhm of 4 cm^{-1}. As shown in Figures 1 and 2, the vibrational frequencies and intensities of the experimental infrared and Raman spectra of SBFL are quite nicely reproduced by the DFT calculations showing almost a one-to-one correspondence. However, the DFT method

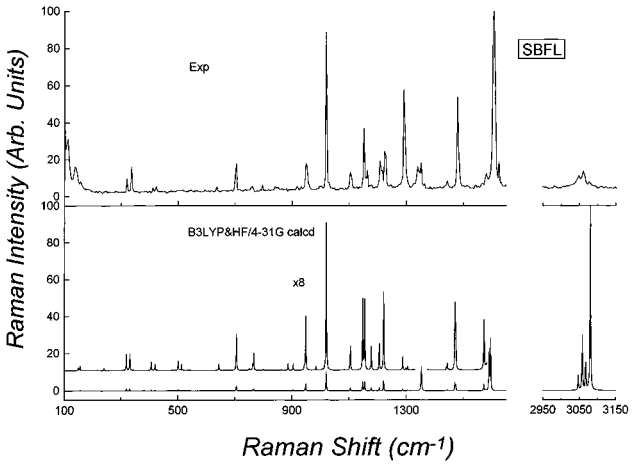


Figure 2. Comparison of the experimental (upper) and calculated (lower) Raman spectra of 9,9′-spirobifluorene.

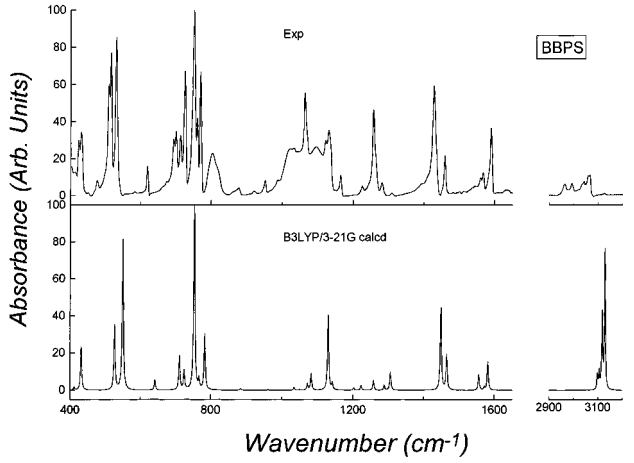


Figure 3. Comparison of the experimental (upper) and calculated (lower) infrared spectra of bis(2,2′-biphenylene)silane.

slightly overestimates the vibrational frequencies above 2950 cm^{-1}, corresponding to the C−H stretching vibration, and greatly overestimates the infrared intensity of the C−H stretching vibration. It is noticed in Figures 2, 4, and 6 that the theoretical Raman intensities are extracted from the ab initio HF calculation since the DFT calculation using the Gaussian 94 program does not produce Raman intensity. The HF Raman intensities are not consistent with the experimental ones in the whole range. However, the experimental Raman intensity ratios below 1650 cm^{-1} are quite correctly reproduced by the HF calculation.

For BBPS and BBPG, some discrepancy in the peak position and intensity is observed between the experimental and theoretical spectra, as indicated in Figures 3−6. Especially, in the region above 2950 cm^{-1}, discrepancy between theory and experiment is appreciably observed in the peak positions and intensities.

As shown in Figures 7 and 8, some frequencies and intensities of SBFL are quite close to those of BBPS and BBPG. However, significant differences are observed in the IR intensities of the fundamentals at 1131, 1567, and 1590 cm^{-1} in BBPS and in those at 1120, 1570, and 1585 cm^{-1} in BBPG. All the frequencies are related to the in-plane CH and CCC bending and M−C_4 (M = C, Si, Ge) stretching vibrational modes. The DFT theory shows that the sizable differences in the IR intensities are caused by the differences in the electronegativities of C (2.55), Si (1.90), and Ge (2.01). The effect is greatly

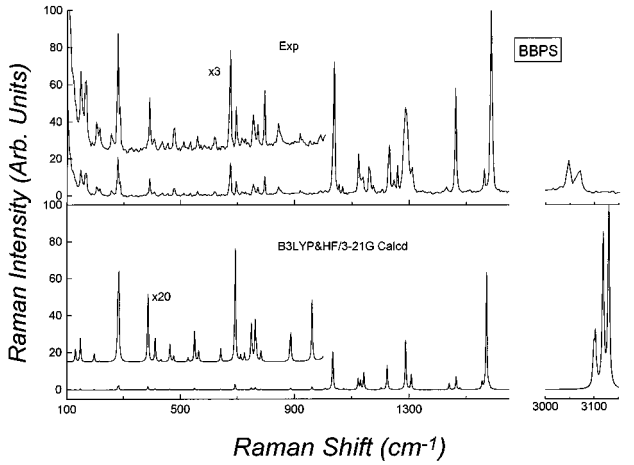


Figure 4. Comparison of the experimental (upper) and calculated (lower) Raman spectra of bis(2,2′-biphenylene)silane.

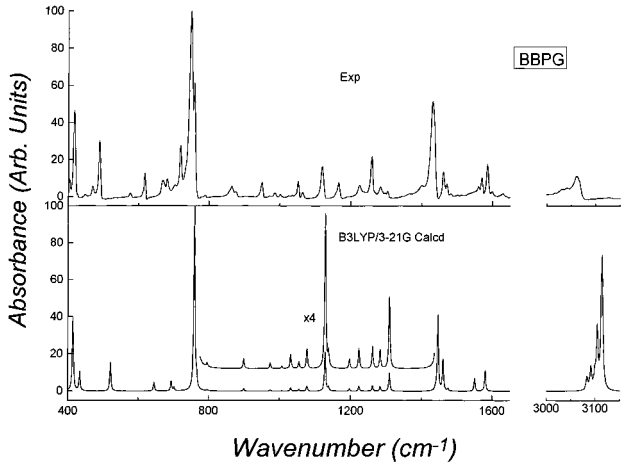


Figure 5. Comparison of the experimental (upper) and calculated (lower) infrared spectra of bis(2,2′-biphenylene)germane.

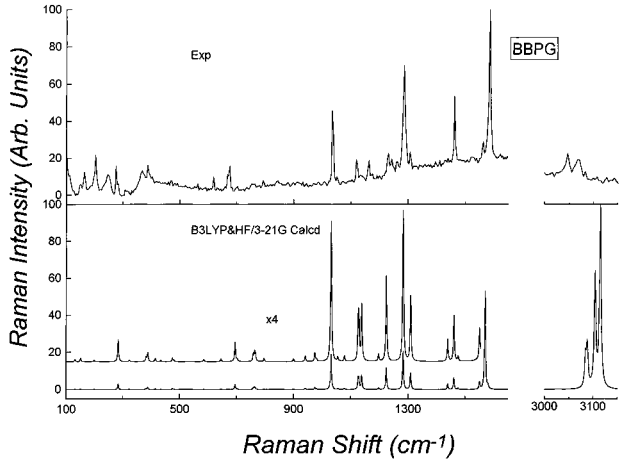


Figure 6. Comparison of the experimental (upper) and calculated (lower) Raman spectra of bis(2,2′-biphenylene)germane.

influenced in the M−C_4 (M = Si and Ge) antisymmetric stretching vibrations, in which the electric dipole moments of the molecules are increased. This is further discussed below.

Under D_{2d} symmetry, quantum mechanical calculation indicates that the molecules include 88 fundamentals having various symmetries of $20a_1 + 9a_2 + 10b_1 + 20b_2 + 29e$. Identification of some of the fundamentals is straightforward due to the well-separated spectral positions and to the excellent agreement in the IR and Raman intensity ratios between theory and experi-

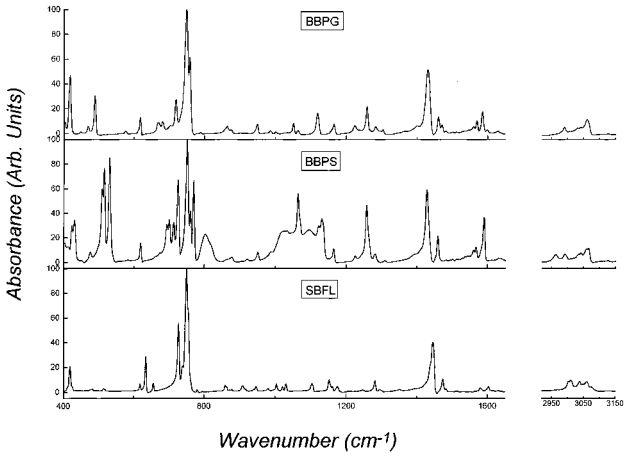


Figure 7. Comparison of the experimental infrared spectra of 9,9′-spirobifluorene, bis(2,2′-biphenylene)silane, and bis(2,2′-biphenylene)-germane.

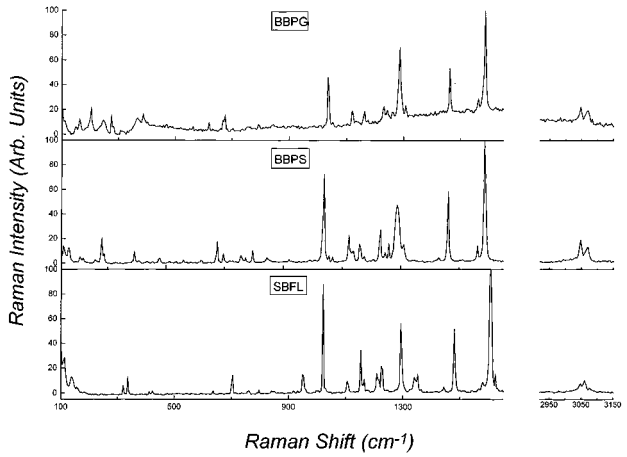


Figure 8. Comparison of the experimental Raman spectra of 9,9′-spirobifluorene, bis(2,2′-biphenylene)silane, and bis(2,2′-biphenylene)-germane.

ment. However, straightforward identification of fundamentals of BBPS and BBPG is not relatively feasible due to the discrepancy between theory and experiment in the peak position and intensity.

Almost all the modes are delocalized over the whole molecule and thus cannot be assigned to several local bonds. This is a characteristic feature of cyclic compounds, particularly aromatic compounds.[28] Therefore we provide in Tables 1 and 2 only the approximate mode descriptions.

9,9′-Spirobifluorene. The scaled fundamentals for SBFL are listed in Table 1 together with the experimental fundamentals. The uniform scaling factors of 0.893 and 0.958 are used for HF/4-31G and B3LYP/4-31G, respectively, the factor of 0.893 has been used in our previous calculations on fluorene,[22] pyrrole,[23] and carbazole,[23] and the factor of 0.958 has been used by Langhoff and has been verified as one of the good scaling factors.[21] The theoretical peak positions shown in Figures 1 and 2 are scaled by 0.958.

The rms deviations of the scaled frequencies from experiment turned out to be 22.80 cm^{-1} for HF/4-31G and 8.82 cm^{-1} for B3LYP/4-31G. It is noticed that the comparison between theory and experiment is made for 50 frequencies listed in Table 1, and the fundamentals are assigned on the basis of this DFT calculation. It is shown in this study that for the 50 experimental frequency data, the scaling factors of 0.891 for the HF calculation and 0.961 for the DFT calculation slightly better

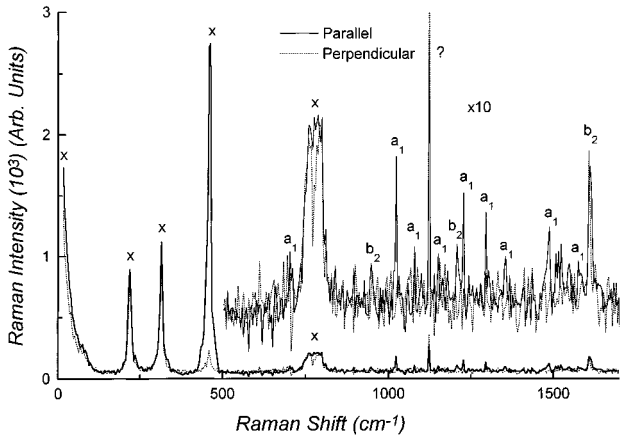


Figure 9. Raman spectra of the saturated solution of 9,9′-spirobifluorene in CCl_4. "x" refers to the solvent peaks. The spectra denoted by the solid and dotted lines were obtained with the electric vector of the scattered light parallel and perpendicular to the electric vector of the incident light, respectively.

reproduce the experimental fundamentals with the rms deviations of 22.63 and 8.30 cm^{-1}, respectively. Since these scaling factors are quite close to the previously used scaling factors by Langhoff,[21] we confirmed that our assignment of the vibrational frequencies and their modes are correctly made and that the DFT method can correctly estimate the fundamentals of the spiro compounds. It is verified again that the DFT method reproduces fundamentals much better than does the HF method. Our frequencies scaled with the reported factor by Langhoff[21] are in excellent agreement with experiment as shown in Table 1.

a_1 Modes. Under D_{2d} symmetry, the SBFL molecule involves 20 a_1 modes. Among the fundamentals, 15 fundamentals that we identify as a_1 fundamentals are 336, 424, 704, 760, 1020, 1088, 1152, 1176, 1224, 1297, 1352, 1444, 1480, 1580, and 1608 cm^{-1}. Among these, the fundamentals at 1020, 1224, 1297, and 1480 cm^{-1} are more or less intense in the Raman spectrum (Figure 9), and thus the modes could be double-checked to be a_1 modes by the depolarization measurement in the solution Raman spectra using a saturated solution in CCl_4. The depolarization ratios measured experimentally are indicated along with the theoretical one in Table 1. It is noticed that the signal-to-noise ratio is quite low since the solubility of SBFL in CCl_4 is very low; therefore only four frequencies with the a_1 mode are safely assigned by the depolarization method.

It is shown in the B3LYP calculation that most of the a_1 fundamentals involve totally symmetric C−H and CCC in-plane bending and stretching modes.

a_2 Modes. Identification of the a_2 fundamentals is impossible here since their modes are infrared and Raman inactive. The DFT calculation indicates that most of the fundamentals correspond to ring torsion and out-of-plane C−H and C−C−C bending modes.

b_1 Modes. Among the 10 fundamentals attributable to b_1, only six fundamentals are identified as b_1 mode. These are 48, 156, 320, 796, 916, and 1004 cm^{-1}. Most of the fundamentals involve C−H out-of-plane bending and ring torsion modes.

b_2 Modes. Among the 20 b_2 modes, only 12 modes are identified. These are 412, 657, 948, 1021, 1104, 1208, 1295, 1351, 1446, 1480, 1581, and 1628 cm^{-1}. Most of the vibrations include C−H in-plane bending and stretching and ring deformation modes.

e Modes. Among the 29 fundamentals with the e mode, 17 fundamentals are identified as the e mode. These are 419, 482, 514, 618, 636, 727, 750, 908, 946, 1004, 1031, 1164, 1176,

TABLE 1: Comparison of the Experimental and Calculated Vibrational Frequencies of 9,9-Spirobifluorene[a]

		HF/4-31G				B3LYP/4-31G		exptl				
sym	no.[b]	freq	I_{IR}	I_{Ram}	DP[c]	freq	I_{IR}	freq	I_{IR}	I_{Ram}	DP[c]	approximate[d] type of mode
a_1	7	150	0	0.2	0.35	150	0					ring defm
	14	330	0	1	0.01	331	0	336		16		ip CH and CCC bend
	16	419	0	0.6	0.23	420	0	424		5		ring defm
	32	705	0	3	0.08	705	0	704		18		ip CH and CCC bend
	40	765	0	1	0.48	766	0	760		6		ip CH and CCC bend
	60	1013	0	10	0.01	1020	0	1020		89	~0	ip CH and CCC bend
	68	1083	0	0.06	0.01	1083	0	1088		5		ip CH and CCC bend
	70	1144	0	6	0.06	1148	0	1152		37		ip CH and CCC bend
	72	1154	0	2	0.21	1178	0	1176		6		ip CH and CCC bend
	76	1197	0	6	0.01	1221	0	1224		25	~0	ring str, ip CH bend
	80	1288	0	0.06	0.04	1298	0	1297			~0	ip CH and CCC bend
	85	1308	0	15	0.02	1354	0	1352		18		ip CH and CCC bend
	87	1452	0	0.6	0.47	1444	0	1444		8		ip CH and CCC bend
	90	1482	0	5	0.02	1471	0	1480		54	~0	ip CH and CCC bend
	97	1587	0	3	0.28	1573	0	1580		12		ip CH and CCC bend
	101	1620	0	35	0.35	1596	0	1608		100		ip CH and CCC bend
	105	2985	0	2	0.73	3048	0					CH str
	108	2995	0	27	0.75	3058	0					CH str
	113	3005	0	11	0.50	3068	0					CH str
	117	3017	0	100	0.01	3080	0					totally sym CH str
a_2	6	134	0	0	0.75	134	0					ring tor
	12	284	0	0	0.75	275	0					ring tor
	19	453	0	0	0.75	440	0					ring tor
	25	580	0	0	0.75	565	0					ring tor
	35	774	0	0	0.75	740	0					oop CH and CCC bend
	41	822	0	0	0.75	785	0					oop CH and CCC bend
	45	929	0	0	0.75	876	0					oop CH bend
	49	1005	0	0	0.75	942	0					oop CH bend
	54	1051	0	0	0.75	983	0					oop CH and CCC bend
b_1	3	49	0	2	0.75	47	0	48		22		ring tor
	8	158	0	0.4	0.75	156	0	156		8		ring tor
	13	329	0	1	0.75	319	0	320		10		ring tor
	22	516	0	0.8	0.75	501	0					oop CH and CCC bend
	26	587	0	0	0.75	574	0					ring tor
	39	796	0	0.5	0.75	762	0					oop CH bend
	42	836	0	0.1	0.75	800	0	796		6		oop CH and CCC bend
	46	941	0	0.6	0.75	886	0	916		5		oop CH bend
	50	1006	0	0.4	0.75	943	0					oop CH and CCC bend
	55	1051	0	0.3	0.75	984	0	1004		6		oop CH and CCC bend
b_2	9	217	0.4	0.05	0.75	216	0.4					ring defm
	15	405	0.7	0.7	0.75	407	1	412		5		ring defm
	31	666	5	0	0.75	665	5	657	7			ip CH and CCC bend
	36	747	0.1	0.1	0.75	748	0.05					ip CH and CCC bend
	53	952	0.7	4	0.75	948	0.4	948	5	18		ip CH and CCC bend
	61	1014	1	3	0.75	1020	2	1021	5	?		ip CH and CCC bend
	67	1099	2	2	0.75	1105	3	1104	7	13		ip CH and CCC bend
	71	1151	0.01	0.1	0.75	1174	0.2					ip CH bend
	75	1197	0.1	2	0.75	1206	2	1208		19		$C(sp^3)-C$ str, ip CH and CCC bend
	77	1227	1	0.6	0.75	1222	6					ip CH and CCC bend
	81	1282	5	0.1	0.75	1299	0.2	1295	2			ip CH and CCC bend
	84	1310	0.2	9	0.75	1352	2	1351	2			ip CH and CCC bend
	86	1451	35	0.2	0.75	1441	29	1446	40			ip CH and CCC bend
	93	1487	0.1	3	0.75	1474	0.01	1480		?		ip CH and CCC bend
	96	1585	1	2	0.75	1572	1	1581	4			ip CH and CCC bend
	98	1616	1	28	0.75	1591	1	1628		18	~1	ip CH and CCC bend
	104	2985	0.06	0.6	0.75	3048	0.5					CH str
	109	2995	0.07	10	0.75	3058	1					CH str
	112	3005	100	0.4	0.75	3068	100					CH str
	116	3016	13	27	0.75	3080	9					CH str
e	1	47	0.01	2	0.75	46	0.01					ring tor and defm
	4	93	1	0.003	0.75	92	0.6					ring tor and defm
	10	244	2	0.2	0.75	240	2					ring tor, ip (CH+CCC) bend
	17	436	5	0.01	0.75	424	3	419	21			ring tor
	20	492	0.2	0.04	0.75	481	0.4	482	3			ring tor and defm
	23	514	0.6	0.5	0.75	513	0.5	514	3			ring tor, ip (CH+CCC) bend
	27	633	2	0	0.75	629	2	618	7			ip CH and CCC bend
	29	650	8	0.5	0.75	644	7	636	29	5		ring tor, ip (CH+CCC) bend
	33	757	9	0.002	0.75	735	18	727	56			oop CH and CCC bend
	37	780	99	0.1	0.75	752	57	750	100			oop CH bend
	43	898	0.01	0.07	0.75	864	0.01					oop CH bend

TABLE 1 (Continued)

sym	no.[b]	HF/4-31G freq	HF/4-31G I_{IR}	HF/4-31G I_{Ram}	HF/4-31G DP[c]	B3LYP/4-31G freq	B3LYP/4-31G I_{IR}	exptl freq	exptl I_{IR}	exptl I_{Ram}	exptl DP[c]	approximate[d] type of mode
	47	936	1	0.6	0.75	904	1	908	5			ip (CH+CCC) bend, oop (CH+CCC) bend
	51	1001	0.2	0.3	0.75	947	0.2	946	5			oop CH and CCC bend
	56	1009	2	0.04	0.75	985	0.02					oop CH and CCC bend
	58	1037	2	0.04	0.75	1005	1	1004	7			ip CH and CCC bend
	62	1051	0.01	0.02	0.75	1035	2	1031	7			ip CH and CCC bend
	65	1101	0.1	0.07	0.75	1103	0.00					ip CH and CCC bend
	69	1138	6	6	0.75	1155	0.06	1164	14			ip CH and CCC bend
	73	1164	0.03	0.001	0.75	1179	2	1176	5			ip CH and CCC bend
	78	1225	3	1	0.75	1288	6	1282	9			ip CH and CCC bend
	82	1304	2	0.3	0.75	1305	0.3					ip CH and CCC bend
	88	1456	23	0.08	0.75	1449	19	1446	?			ip CH and CCC bend
	91	1483	11	0.9	0.75	1473	5	1474	10			ip CH and CCC bend
	94	1590	0.1	0.06	0.75	1570	0.02					ip CH and CCC bend
	99	1614	0.9	2	0.75	1594	1	1604	5			ip CH and CCC bend
	102	2983	3	9	0.75	3047	3					CH str
	106	2993	10	2	0.75	3056	8					CH str
	110	3004	0	11	0.75	3067	0.2					CH str
	114	3016	50	0.7	0.75	3079	51					CH str

[a] Vibrational frequencies in cm^{-1}. [b] Mode numbers are extracted from the output of the DFT calculation. [c] Depolarization ratio. [d] Approximate mode descriptions are extracted from output of the DFT calculation. ip refers to in-plane; oop out-of-plane; tor to torsion, and the modes assigned are sorted in the order of their contributions to the vibrational motions.

TABLE 2: Comparison of the Infrared and Raman Vibrational Frequencies and Intensities of 9,9′-Spirobifluorene (SBFL), Bis(2,2′-biphenylene)silane (BBPS), and Bis(2,2′-biphenylene)germane (BBPG)[a]

sym	freq (int %) SBFL	freq (int %) BBPS	freq (int %) BBPG	approximate[b] type of mode
			Infrared	
e	750 (100)	751 (100)	749 (100)	oop(CH + CCC) bend, M-C_4 almost not in vibration
b_2	1104 (7)	1131 (35)	1120 (16)	ip(CH + CCC) bend, M−C_4 str
e	1282 (9)	1309 (1)	1303 (3)	ip(CH + CCC) bend, M−C_4 rocking
e	1446 (?)	1428 (59)	1430 (52)	ip(CH + CCC) bend, M−C_4 rocking
b_2	1446 (40)	1459 (22)	1461 (14)	ip(CH + CCC) bend, M−C_4 scissoring
b_2	1581 (4)	1567 (13)	1570 (10)	ip(CH + CCC) bend, M−C_4 str and scissoring
e	1604 (5)	1590 (37)	1585 (18)	ip(CH + CCC) bend, M−C_4 str and rocking
			Raman	
a_1	704 (18)	675 (18)	675 (16)	ip(CH + CCC) bend, M−C_4 scissoring
a_1	1020 (89)	1039 (72)	1035 (46)	ip(CH + CCC) bend, M−C_4 str
b_2	1104 (7)	1139 (10)	1131 (11)	ip(CH + CCC) bend, M−C_4 str
a_1	1152 (37)	1123 (23)	1119 (19)	ip(CH + CCC) bend, M−C_4 str
e	1164 (14)	1159 (16)	1163 (19)	ip(CH + CCC) bend, M−C_4 str
a_1	1224 (25)	1231 (27)	1231 (23)	ip(CH + CCC) bend, M−C_4 str
a_1	1480 (54)	1463 (58)	1463 (53)	ip(CH + CCC) bend, M−C_4 scissoring
a_1	1580 (12)	1563 (14)	1563 (29)	ip(CH + CCC) bend, M−C_4 scissoring
a_1	1608 (100)	1587 (100)	1587 (100)	ip(CH + CCC) bend, M−C_4 scissoring

[a] Vibrational frequencies in cm^{-1}. [b] Approximate mode descriptions are extracted from output of the DFT calculation. ip refers to in-plane; oop to out-of-plane.

1282, 1446, 1474, and 1604 cm^{-1}. Most of the fundamentals involve ring deformation and in-plane C−H and CCC bending and C−H stretching modes.

Bis(2,2′-biphenylene)silane. We could assign only 25 fundamentals on the basis of the HF and DFT calculations. We have optimized the scaling factors by minimizing the rms deviation to yield 0.904 and 0.973 for HF/3-21G and B3LYP/3-21G, respectively. When we use these scaling factors, the rms deviations of the scaled computed frequencies from experiment are found to be 20.82 and 8.52 cm^{-1} for HF/3-21G and B3LYP/3-21G, respectively. It is noticed that since the scaling factors are optimized using the fundamentals below 1650 cm^{-1}, the rms values are relatively low. Figures 3 and 4 are the results scaled by 0.973.

a_1 Modes. Among the 20 fundamentals, eight fundamentals that we identify as a_1 fundamentals by Raman spectroscopy are 391, 675, 1039, 1123, 1287, 1463, 1563, and 1587 cm^{-1}. As shown in Figure 8, the Raman intensities are almost invariant with respect to the polarity change of the Si−C_4 bonds due to the presence of the low-electronegative central atom.

a_2 Modes. Identification of the a_2 vibrational frequencies is also impossible here since their modes are infrared and Raman inactive.

b_1 Modes. Among the 10 fundamentals attributable to b_1, only one frequency 279 cm^{-1} is identified as a b_1 mode.

b_2 Modes. Among the 20 b_2 modes, only five modes are identified. These are 530, 770, 1139, 1459, and 1567 cm^{-1}. The infrared intensities corresponding to 1131 and 1567 cm^{-1} are greatly enhanced in comparison with those of SBFL. The DFT calculation indicates that the modes involve the Si−C_4 antisymmetric stretching frequencies, of which vibrations change the electric dipole moment.

e Modes. Among the 29 e frequencies, only 11 frequencies are identified as the e mode. These are 407, 430, 479, 515,

619, 751, 761, 1159, 1258, 1428, and 1590 cm^{-1}. As shown in Figure 7 and Table 2, the IR intensity of 751 cm^{-1} is invariant with the change of the central atom. This is because the mode involves only the out-of-plane C−H vibration; that is the Si−C_4 subunit is not in vibration. The IR intensity corresponding to 1590 cm^{-1} is, however, enhanced since the Si−C_4 vibration involves the stretching and rocking modes.

Bis(2,2′-biphenylene)germane. We could safely assign only 26 fundamentals. The uniform scaling factors of 0.900 and 0.968 for HF/3-21G and B3LYP/3-21G, respectively, are the best values to minimize the rms deviations of the experimental fundamentals from theory.

The rms deviations of computed frequencies from experiment turned out to be 22.90 and 15.43 cm^{-1} for HF/3-21G and B3LYP/3-21G, respectively.

a_1 Modes. Among the 20 fundamentals, nine fundamentals that we identify as a_1 fundamentals are 275, 387, 675, 1035, 1119, 1231, 1287, 1563, and 1587 cm^{-1}. The intensities of the Raman bands at 675, 1035, 1119, 1231, 1463, 1563, and 1587 cm^{-1} listed in Table 2 are almost invariant with the change of the central atom, indicating that the dipole changes do not affect the Raman intensity.

a_2 Modes. Identification of the a_2 vibrational frequencies is also impossible here since their modes are infrared and Raman inactive.

b_1 Modes. Among the 10 fundamentals attributable to b_1, only one frequency, 275 cm^{-1}, is identified as a b_1 mode.

b_2 Modes. Among the 20 b_2 modes, only seven modes can be identified. These are 681, 758, 1051, 1120, 1307, 1461, and 1570 cm^{-1}. The IR intensities of fundamentals at 1120 and 1570 cm^{-1} are enhanced since the Ge−C_4 vibrations include a Ge−C antisymmetric stretching mode.

e Modes. Among the 29 e fundamentals, nine fundamentals are identified as the e mode. These are 447, 488, 618, 668, 749, 1163, 1303, 1430, and 1585 cm^{-1}. As shown in Figure 5 and Table 2, the IR intensity of 749 cm^{-1} is invariant with the change of the central atom. However, the IR intensity of fundamental at 1585 cm^{-1} is increased due to the presence of the low electronegative Ge atom.

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