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Article

IR and Raman Vibrational Assignments for Metal-free Phthalocyanine from Density Functional B3LYP/6-31G(d) Method

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Vibrational (IR and Raman) spectra for the metal-free phthalocyanine (H_2Pc) have been comparatively investigated through experimental and theoretical methods. The frequencies and intensities were calculated at density functional B3LYP level using the 6-31G(d) basis set. The calculated vibrational frequencies were scaled by the factor 0.9613 and compared with the experimental result. In the IR spectrum, the characteristic IR band at 1008 cm^{-1} is interpreted as C—N (pyrrole) in-plane bending vibration, in contrast with the traditional assigned N—H in-plane or out-of-plane bending vibration. The band at 874 cm^{-1} is attributed to the isoindole deformation and aza vibration. In the Raman spectrum, the bands at 540, 566, 1310, 1340, 1425, 1448 and 1618 cm^{-1} are also re-interpreted. Assignments of vibrational bands in the IR and Raman spectra are given based on density functional calculations for the first time. The present work provides valuable information to the traditional empirical assignment and will be helpful for further investigation of the vibration spectra of phthalocyanine analogues and their metal complexes.

Keywords　phthalocyanine, DFT method, IR spectra, Raman spectra

Introduction

IR and Raman spectroscopy techniques have proved to be versatile for studying the intrinsic properties of phthalocyanine compounds.[1-24] Since the first report of Cannon and Sutherland[1] in 1951, infrared spectrum of metal-free phthalocyanine (H_2Pc) has been recorded by different research groups.[3-10] However, assignments of the IR bands were still made mainly on the basis of empirical comparison of experimental results with those of related macro rings such as benezene, isoindole and pyrrole till 1998.[3,10] Contradictive assignments have appeared for the assignment of the characteristic band at 1008 cm^{-1} and another band at 874 cm^{-1}.[2-4,7,9,10] The vibrations in the Raman spectra of H_2Pc[11] and metal phthalocyanine complexes[12] have also been studied through empirical comparison with the spectroscopic results of porphyrin, indole and pyrrole in 1982 and 1997, respectively, but detailed assignment was not reached.

Vibrational spectroscopic investigation with the help of quantum chemistry calculations attracts more research interest in recent years. The frequencies of H_2Pc have been calculated at the Hartree-Fock level using the 3-21G basis set and the calculated frequencies below 700 cm^{-1} were compared with the experimental data.[13] However, it seems that the results need further improvement because of the neglect of electron correlation in the Hartree-Fock calculation. Gong and co-workers studied the infrared spectra of H_2Pc at the B3LYP/3-21G and B3LYP/6-31G(d) levels and published the simulated spectra in 2002,[14] however, no assignment of the spectra was tried in their report.

In the present paper, IR and Raman frequencies and intensities were calculated at the DFT B3LYP level using the 6-31G(d) basis set. The calculated frequencies were scaled by the factor 0.9613[15] and compared with the experimental data. Assignments of vibrational modes for H_2Pc are thus tried for the first time through comparison between experimental and density functional calculation results.

Experimental

Phthalonitrile was obtained from Aldrich Chemical Company. 2-Dimethylaminoethanol and methanol were obtained from Beijing Chemical Reagent Company and used as received. Unsubstituted metal-free H_2Pc was prepared according to the reported procedures.[24] IR spectrum was recorded from KBr disks using a Bio-Rad FTS165 spectrometer in the range of 400—4000 cm^{-1} with resolution of 2 cm^{-1} and Raman spectrum was recorded with the resolution of 4 cm^{-1} using a Renishaw Raman Microprobe, equipped with a Spectra Physics

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model 127 He—Ne laser excitation source emitting at a wavelength of 632.8 nm.

Computational method

The structure of H_2Pc and the atom numbering are shown in Figure 1 according to which the input structure is deduced. The hybrid density functional B3LYP method was used for both geometry optimization and frequency/intensity calculations. In all cases, the 6-31G(d) basis set was used. The Berny algorithm using redundant internal coordinates[25] was employed in energy minimization and the tight convergence criteria were used. D_{2h} symmetry in the input structure was detected and then enforced by the program. Using the energy-minimized structure generated in the previous step, normal coordinate analysis was carried out. The IR and Raman vibrational frequencies and their intensities were calculated by using the same method and basis set. All calculations were carried out using Gaussian98 program[26] on a Pentium IV computer.

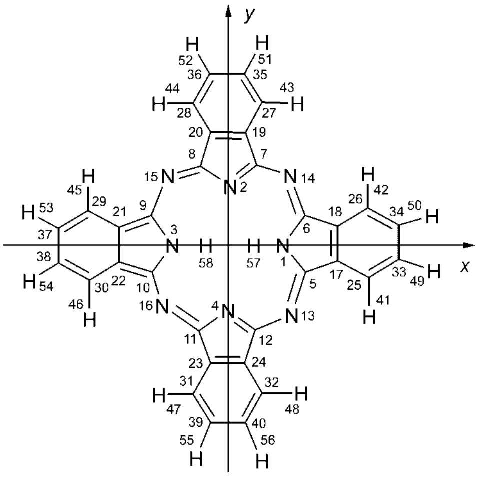

Figure 1 Structure and atom numbering of H_2Pc.

The primarily calculated vibrational frequencies were scaled by the factor 0.9613 which was recommended in previous research work.[15] Detailed assignment was given according to the comparison between the theoretical data and the experimental results. The normal mode descriptions were obtained with assistance of animated pictures produced based on the normal coordinates.

Results and discussion

Energy-minimized structure

The energy-minimized structure of H_2Pc molecule calculated at B3LYP/6-31G(d) level is D_{2h} symmetry. No imaginary vibration is predicted in the following frequency calculation, indicating that the energy minimized structure is a true energy minimum. Corresponding structural parameters are listed in Table 1 together with the experimental data.[27] The structural parameters of the minimum-energy geometry not only agree with previous calculations[14] but also are in good correspondence with the experimental values.[27] Normal coordinate analysis has been performed based on this minimum-energy geometry.

Fundamental vibrational wavenumbers (Infrared and Raman spectra)

The H_2Pc molecule has 168 normal vibrational modes. The vibrational representation found from the calculation result is as follows:

$$\Gamma_{\text{vib}} = 28B_{1u}(\text{IR}) + 28B_{2u}(\text{IR}) + 15B_{3u}(\text{IR}) + 13B_{1g}(\text{Ra}) + 14B_{2g}(\text{Ra}) + 28B_{3g}(\text{Ra}) + 13A_u + 29A_g(\text{Ra})$$

IR and Ra represent infrared active and Raman active modes, respectively. B_{1u}, B_{2u} and B_{3u} modes are infrared active, while B_{1g}, B_{2g}, B_{3g} and A_g modes are Raman active. The A_u modes are vibrationally inactive. According to these analyses, there are 71 infrared and 84 Raman vibrations for H_2Pc.

Table 1 Structure parameters of the optimized geometry and the experimental data

Parameter[a]	Calcd[b]	Exp.[c]	Parameter[a]	Calcd[b]	Exp.[c]
N(1)—H(57)	1.014	0.93	N(3)—H(58)	1.014	0.93
N(1)—C(6)	1.378	1.38	N(2)—C(7)	1.365	1.38
N(3)—C(9)	1.378	1.37	N(2)—C(8)	1.365	1.36
C(6)—N(14)	1.318	1.30	C(7)—N(14)	1.336	1.31
C(9)—N(15)	1.318	1.31	C(8)—N(15)	1.336	1.34
C(6)—C(18)	1.453	1.49	C(7)—C(19)	1.467	1.47
C(9)—C(21)	1.453	1.46	C(8)—C(20)	1.467	1.46
C(17)—C(18)	1.414	1.41	C(19)—C(20)	1.404	1.40
C(18)—C(26)	1.397	1.37	C(19)—C(27)	1.393	1.39
C(21)—C(29)	1.397	1.40	C(20)—C(28)	1.393	1.39
C(26)—C(34)	1.392	1.41	C(27)—C(35)	1.397	1.39

Continued

Parameter[a]	Calcd[b]	Exp.[c]	Parameter[a]	Calcd[b]	Exp.[c]
C(29)—C(37)	1.392	1.38	C(28)—C(36)	1.397	1.38
C(33)—C(34)	1.410	1.43	C(35)—C(36)	1.406	1.42
C(26)—H(42)	1.085	1.11	C(27)—H(43)	1.086	1.04
C(29)—H(45)	1.085	1.02	C(28)—H(44)	1.086	1.14
C(34)—H(50)	1.086	1.05	C(35)—H(51)	1.087	1.13
C(37)—H(53)	1.086	1.06	C(36)—H(52)	1.087	1.05
C(5)-N(1)-C(6)	112.5	110	C(7)-N(2)-C(8)	106.9	108
N(1)-C(6)-C(18)	106.1	107	N(2)-C(7)-C(19)	110.9	109
N(3)-C(9)-C(21)	106.1	109	N(2)-C(8)-C(20)	110.9	110
N(1)-C(6)-N(14)	128.2	131	N(2)-C(7)-C(14)	127.7	128
N(3)-C(9)-N(15)	128.2	127	N(2)-C(8)-N(15)	127.7	127
C(6)-N(14)-C(7)	123.8	125	C(8)-N(15)-C(9)	123.8	122
C(6)-C(18)-C(17)	107.6	106	C(7)-C(19)-C(20)	105.6	106
C(9)-C(21)-C(22)	107.6	107	C(8)-C(20)-C(19)	105.6	106
C(6)-C(18)-C(26)	131.4	131	C(7)-C(19)-C(27)	133.1	131
C(9)-C(21)-C(29)	131.4	133	C(8)-C(20)-C(28)	133.1	134
C(18)-C(26)-C(34)	117.8	117	C(19)-C(27)-C(35)	117.6	117
C(21)-C(29)-C(37)	117.8	118	C(20)-C(28)-C(36)	117.6	119
C(18)-C(26)-H(42)	120.5	123	C(19)-C(27)-H(43)	120.8	120
C(21)-C(29)-H(45)	120.5	123	C(20)-C(28)-H(44)	120.8	118
C(26)-C(34)-C(33)	121.2	120	C(27)-C(35)-C(36)	121.1	121
C(29)-C(37)-C(38)	121.2	122	C(28)-C(36)-C(35)	121.1	120
C(26)-C(34)-H(50)	119.6	122	C(27)-C(35)-H(51)	119.6	118
C(29)-C(37)-H(53)	119.6	123	C(28)-C(36)-H(52)	119.6	120

[a] Bond lengths in ($\times 10^{-1}$) nm, angles in degree. [b] Present result. [c] Quoted from Ref. 27.

Infrared spectra

Since there are only few weak bands in the range from 1800 cm^{-1} to 4000 cm^{-1}, the recorded IR spectrum of H_2Pc in the range of fundamental frequencies 400—1800 cm^{-1} is shown in Figure 2. The experimental frequencies and corresponding IR active B_{1u}, B_{2u} and B_{3u} modes are listed in Table 2. An IR spectrum was simulated from the calculated frequency and intensity data by adding a Lorentzian lineshape with a half-width at half-maximum of 6 cm^{-1}. The simulated IR spectrum obtained is also comparatively shown in Figure 2. The correlation between the experimental and calculated IR frequencies is good, while the intensity correlation is not very good. The calculated modes were assigned to experimental bands primarily based on frequencies. However, in the case that there are more than one possible vibration modes, the intensity data were used as additional evidence to assist assignment.

The bands above 3000 cm^{-1} are C—H and N—H stretching vibrations according to our calculation. The asymmetrical N—H stretching mode at 3289 cm^{-1} in the IR spectrum of H_2Pc is predicted at 3423 cm^{-1} using 6-31G(d) basis set. The C—H stretching vibrations observed at 3050 and 3071 cm^{-1} consisting of eight vibrational modes are predicted in the range of 3064—3100 cm^{-1}. However, the origin of the band at 2925 cm^{-1} is unknown.

The most intense band at 1008 cm^{-1} has been regarded as a characteristic band of metal-free H_2Pc[9] and used as an effective method to check the purity of metallophthalocyanine complexes.[16] In the previous studies,[3,4,8-10] this band was usually assigned to N—H

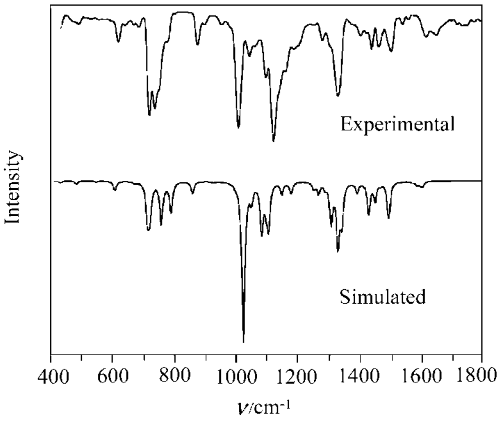

Figure 2 Experimental and simulated IR spectra of H_2Pc.

Table 2 IR frequencies (cm^{-1}) and their assignments

Exp.	B_{1u}	B_{1u} Int.	B_{2u}	B_{2u} Int.	B_{3u}	B_{3u} Int.
					19.74	0.002
					37.50	1.312
	117.7	4.096	116.5	3.245	133.3	0.3115
					214.6	4.148
	271.7	8.093	265.4	0.3135	251.5	2.220
					328.2	2.384
					418.2	0.0584
					431.2	7.383
490	482.8	7.477	480.3	3.065		
	545.3	3.253	539.3	0.0307		
618	606.9	27.87	607.2	3.687		
					671.4	5.735
718	717.2	69.39	722.4	67.56	711.8	98.41
					755.4	2.687
735					757.3	140.0
775	771.0	3.691	775.3	0.8252	788.2	106.0
			822.4	0.0242		
874	857.7	41.15				
					922.5	1.601
					928.8	1.953
	997.9	0.3008	998.4	5.594		
1008	1023	544.3				
1044			1031	6.880		
1061	1049	53.81				
1095	1096	62.95	1082	161.3		
1120			1104	140.5		
1159	1148	28.98	1146	11.18		
1185	1171	0.6632	1177	39.12		
1250			1251	22.32		
1277	1266	38.17	1288	18.51		
1305	1304	13.13	1308	125.3		
1329	1329	202.8	1341	125.0		
1402	1391	35.93				
1437			1428	107.1		
1461	1449	63.41				
	1460	0.1313	1468	8.965		
1501	1494	100.4	1491	27.21		
1538			1533	1.929		
	1569	4.300	1584	12.40		
1614	1596	10.98	1603	15.52		
2925						
	3064	7.203	3068	8.820		
3050	3082	50.79	3078	58.83		
3071	3092	20.67	3095	70.41		
	3100	58.06	3097	15.23		
3289	3423	117.9				

in-plane or out-of-plane bending mode by comparing the IR spectra of phthalocyanine and its metal derivatives. According to the present calculated results of H_2Pc, the C—N (pyrrole) in-plane bending mode which shows the strongest absorption at 1023 cm^{-1} indeed contributes to the absorption band at 1008 cm^{-1} of H_2Pc. A N—H in-plane bending mode is predicted at 1031 cm^{-1} coupled with isoindole deformation, which is considered corresponding with the weak band observed at 1043 cm^{-1}.

Shurvell and Pinzuti[3] assigned the intense band at 1008 cm^{-1}, which is absent from the spectra of metalated phthalocyanine derivatives, to N—H in-plane bending mode. However, Sammes[7] found that this absorption was not affected either in position or in intensity upon deuteriation of the central protons in H_2Pc. This fact is in good agreement with our above-described conclusion that the 1008 cm^{-1} band contains the C—N (pyrrole) in-plane bending mode, not the N—H in-plane bending mode. A comparative calculation of the IR spectra of H_2Pc and D_2Pc at B3LYP level using 6-31G(d) basis set reveals that the vibration mode of H_2Pc predicted at 1023 cm^{-1} with relative intensity 544.3 also appears at 1022 cm^{-1} of D_2Pc with relative intensity 532.6, while the vibration mode predicted at 1031 cm^{-1} with relative intensity 6.880 of H_2Pc shifts to 946.4 cm^{-1} with relative intensity 67.00 of D_2Pc.[28] These results clearly interpret the phenomenon observed by Sammes.[7] Therefore we prefer to assign the 1008 cm^{-1} band of H_2Pc to C—N (pyrrole) in-plane bending mode rather than the N—H in-plane bending mode.

According to the present calculation result, the N—H out-of-plane bending mode was predicted at 788.2 cm^{-1}, which was observed at 775 cm^{-1} in the IR spectrum of H_2Pc. In the comparative calculation for D_2Pc,[28] corresponding N—D out-of-plane bending mode was predicted at 563.0 cm^{-1}, which seems to be in line with the band observed at 549 cm^{-1} in the recorded spectrum. These results also support the point of Sammes[7] that the band at 549 cm^{-1} of D_2Pc is N—D out-of-plane bending mode, but the assignment of the N—H out-of-plane bending vibration mode to the band observed at 735 cm^{-1} was not supported.

The band at 886 cm^{-1} in the IR spectra of monomeric phthalocyaninato metal complexes has ever been assigned to metal-nitrogen vibration.[2,4] But this assignment was considered to be unclear according to Shurvell,[3] Clarisse[9] and Janczak[10] because of the appearance of the band at 874 cm^{-1} in the IR spectrum of H_2Pc. In the present work, the animated picture of the 874 cm^{-1} band indicates that it is mainly attributed from isoindole deformation and aza vibration while the relative positions of the four central N atoms are almost not changed. This seems to support the point of Shurvell,[3] Clarisse,[9] Janczak[10] and Jiang.[18] Recent comparative calculations on the vibrational spectra of magnesium phthalocyanine[28] have given more clear information on this IR absorption band. The band at 886 cm^{-1} was found to be isoindole deformation and aza vibration coupled also with metal nitrogen vibration. This may be interpreted as follows:

In the metal-free phthalocyanine, the hydrogen atoms just connect with two pyrrole-nitrogen atoms and have no connection with the other two pyrrole-nitrogen atoms. When the isoindole deformation and aza vibration occur, the hydrogen atoms just move together with the two direct-connected pyrrole-nitrogen atoms without N—H vibration, which was also supported by the calculation results of D_2Pc. While in the metal phthalocyanine complexes, the metal ion is coordinated with the four nitrogen atoms. The vibration ranges of the four nitrogens are different because of symmetry restriction, which causes vibration between metal and nitrogen to occur. Therefore this vibrational mode may still exist in the IR spectra of metal phthalocyanines with small shift, which will show some dependence on metal ionic size. In our recent research over IR spectroscopic data for a series of bis(phthalocyaninato) rare earth complexes,[22] the vibration at 876—887 cm^{-1} was found to be metal size dependent. This gives additional experimental support to the above-mentioned assignment for this vibration mode. Similar trends were also observed for vibrations at 1063—1072 cm^{-1} and 1110—1116 cm^{-1} of the bis(phthalocyaninto) rare earth complexes, which are tentatively considered to come from the bands at 1061 and 1120 cm^{-1} for H_2Pc, respectively.

A line of best fit through a plot of the experimental IR frequencies versus the calculated ones in the range of 400—1800 cm^{-1} is shown in Figure 3. The correlation coefficient and the standard deviation between the experimental and calculated data are 0.9995 and 10.2 cm^{-1}, respectively, indicating that the correlation is very good. The intercept value of the linear regression is -2.46 cm^{-1}, revealing that the systematic error is very small although the line does not have an intercept of zero.

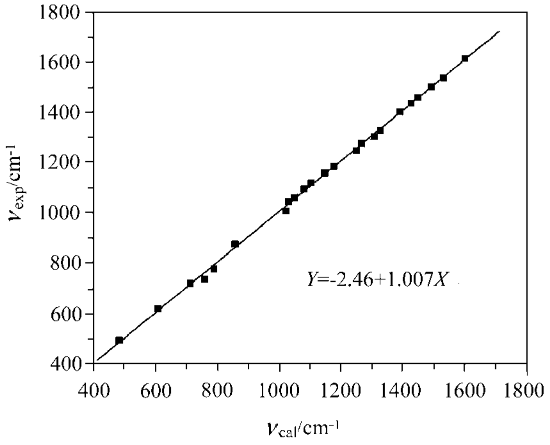

Figure 3 Fit between the experimental and calculated IR data of H_2Pc..

Raman spectra

The experimental Raman frequencies and corresponding Raman active B_{1g}, B_{2g}, B_{3g} and A_g modes are listed in Table 3. A Raman spectrum was simulated from the calculated frequency and intensity data by adding a Lorentzian lineshape with a half-width at half-maximum of 6 cm^{-1}. The simulated Raman spectrum obtained is shown in Figure 4 along with the experimental spectrum. The correlation between the experimental and calculated results is not so good as that of the IR spectra, especially for the intensities. In view of subsequent applications of the vibrational analysis, it is useful to discuss the Raman spectra of H_2Pc in terms of four basic structure moieties: the 16-membered inner ring or macrocycle, the isoindole moieties, pyrrole or benzene groups and C—H or N—H bonds.

Vibrations of the macrocycle

On the basis of comparative method as mentioned above, Aroca and coworkers,[11] have assigned the band

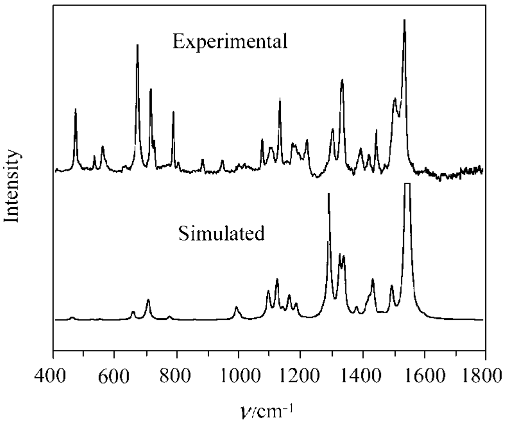

Figure 4 Experimental and simulated Raman spectra of H_2Pc.

Table 3 Raman frequencies (cm^{-1}) and their assignments (λ_{ex}=632.8 nm)

Exp.	A_g	A_g Int.	B_{1g}	B_{1g} Int.	B_{2g}	B_{2g} Int.	B_{3g}	B_{3g} Int.
			56.16	0.2109	49.78	0.35		
	128.4	31.75	123.7	12.74	113.5	10.15	82.17	4.941
							175.0	27.34
	221.3	65.26	229.9	7.482	214.3	9.255	201.9	1.258
			277.8	0.2561	263.7	0.1389		
			417.8	0.1705	418.1	0.0406		
479			485.2	1.163	485.5	1.159	468.5	119.7
540	531.1	19.33						
566	556.4	35.23					556.0	1.663
							589.0	0.4218
			622.3	1.429	626.1	1.321		
					639.5	2.849		
680	664.0	374.5			698.9	17.76	669.7	4.213
721	712.9	924.1	710.9	26.19				
731	752.8	3.785	758.8	2.082	756.5	0.5802		
774			763.9	9.006	765.9	5.064		
795	782.7	145.0					810.2	0.4822
			862.0	3.606	863.3	4.718	871.5	2.462
			922.5	2.209	928.8	0.5213		
			959.2	0.3773	954.1	0.0702		
	998.1	147.0						
1009	998.7	388.2						
1024							1009	151.2
							1068	32.49
							1090	57.65
1082							1099	324.1
1107	1102	933.9						
1111	1128	1782						
1138	1148	315.3						
1179	1168	986.4					1177	57.84
1188							1190	638.4
1227							1221	35.97
							1277	179.3

Continued

Exp.	A_g	A_g Int.	B_{1g}	B_{1g} Int.	B_{2g}	B_{2g} Int.	B_{3g}	B_{3g} Int.
1310	1297	5412					1294	324.9
1340	1331	2420						
	1344	2392						
1398	1386	410.5						
	1416	310.9						
1425							1425	602.9
1448	1437	1638					1459	57.00
							1469	142.1
1513	1499	1312						
1541	1550	17059					1530	6.782
	1569	119.5						
	1585	27.44						
							1596	0.0178
1618							1604	73.62
							3064	209.2
							3068	238.8
	3078	723.2						
	3082	764.8						
	3095	670.7					3092	169.2
	3100	752.8					3097	176.0
	3478	10.74						

at 680 cm^{-1} in the Raman spectrum of H_2Pc to the macrocycle breathing. The intense band at 664.0 cm^{-1} in the simulated spectrum clearly corresponds to this vibration. The bands lying at 566 and 795 cm^{-1}, which are in good accordance with those at 556.4 and 782.7 cm^{-1} in the simulated spectrum, are also assigned to the central macrocycle breathing vibrations.

Vibrations of isoindole moieties

The intense band at 1340 cm^{-1} was previously assigned to C_α—C_β stretching at the pyrrole groups.[11] It seems to correspond with the predicted band peaking at 1331 cm^{-1}. However, according to our calculation, not only the C—C bonds of the pyrrole rings but also the C—C bonds of the benzene rings contribute to the scattering at 1340 cm^{-1}. The shoulder peak at 1310 cm^{-1} also contains the contribution from stretching vibrations of both the C_α—C_β bonds of pyrrole rings and the C—C bonds in the benzene rings. By analogy to the stretching vibrations of the conjugated system in isolated indole being observed at 1487 and 1455 cm^{-1}, the prominent bands at 1450 and 1425 cm^{-1} in the Raman spectrum of H_2Pc were described as isoindole ring stretches.[11] However, according to the present calculation, the band observed at 1448 cm^{-1} should be assigned to the C—H in-plane bending vibrations with contribution also from the C—C stretching vibrations of the benzene rings while the band at 1425 cm^{-1} should be assigned as pyrrole deformation coupled with C—N (aza) stretching vibration.

Vibrations of pyrrole or benzene groups

The typical stretching vibration of the benzene nucleus in isoindole, which corresponds to the peak observed at 1618 cm^{-1}, is predicted at 1604 cm^{-1} based on the present calculation. This result gives additional support to the assignment of Aroca.[11] Both peaks appearing at 540 and 566 cm^{-1} contain stretching vibrations of benzene rings according to our calculation. However, the central 16-membered macrocycle ring is found to stretch and breathe in these two vibrational modes, respectively, in association with the benzene ring stretching. This assignment agrees with the previous work of Aroca,[11] in which the band at 566 cm^{-1} was believed to be due mostly to the benzene group because its relative intensity was increased by approximation to the Soret band.

Vibrations of N—H or C—H bonds

According to the theoretical studies, in the Raman spectrum of H_2Pc, the scatterings ranging from 1082 cm^{-1} to 1227 cm^{-1} are mostly contributed from C—H in-plane bending vibrations, two of which at 1107 and 1111 cm^{-1} are found to contain benzene breathing vibration and the one at 1179 cm^{-1} is found to contain the isoindole stretching vibration. The out-of-plane bending vibrations of C—H and N—H bonds lie mostly in the range of 721—1009 cm^{-1}. The relative intensities of these vibrational modes are very weak. They contribute very little to the strong peaks in this region.

A line of best fit through a plot of the experimental Raman frequencies versus the calculated ones in the range of 400—1800 cm^{-1} is shown in Figure 5. The correlation coefficient and the standard deviation between the experimental and calculated data are 0.9995 and 11.3 cm^{-1}, respectively, also indicating that the correlation is very good. The intercept value of the linear regression is 6.81 cm^{-1}, revealing a very small systematic error of the present assignment.

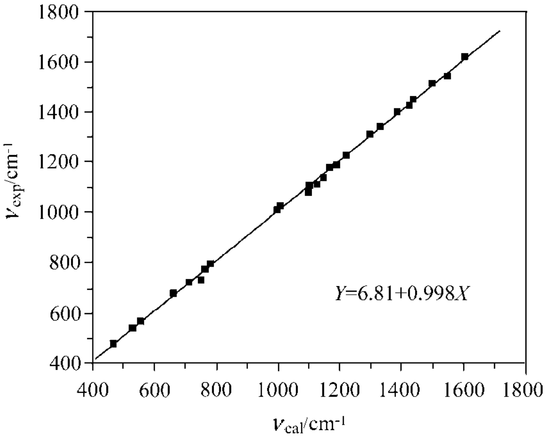

Figure 5 Fit between the experimental and calculated Raman data of H_2Pc.

Conclusions

Assignments of the IR and Raman spectra for H_2Pc have been given for the first time based on density functional calculations. In the IR spectrum, the characteristic absorption band at 1008 cm^{-1} in the IR spectrum is interpreted as C—N (pyrrole) in-plane bending mode in contrast with the traditional empirical assignment of N—H in-plane bending mode. The band at 874 cm^{-1} is assigned as isoindole deformation and aza vibration. In the Raman spectrum, the bands at 540, 566, 1310, 1340, 1425, 1448 and 1618 cm^{-1} are also re-interpreted with assistance from animated pictures. The present work provides valuable information to the traditional empirical assignment for further investigation of the vibration spectra of phthalocyanine analogues and their metal complexes.

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