



Analysis on vibrational spectra of Hexafluorobenzene based on density functional theory calculations

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ARTICLE INFO

Article history:

Received: 25 January 2011;

Received in revised form:

15 February 2011;

Accepted: 28 February 2011;

Keywords

Vibrational analysis,
Hexafluorobenzene,
DFT calculations,
FTIR,
FT-Raman.

ABSTRACT

This work deals with the vibrational spectroscopy of Hexafluorobenzene (HFB) by means of quantum chemical calculations. The FTIR and FT-Raman spectra were measured in the condensed state. The fundamental vibrational frequencies and intensity of vibrational bands were evaluated using density functional theory (DFT) with the standard B3LYP / 6-311+G** basis set combinations, and was scaled using various scale factors which yields a good agreement between observed and calculated frequencies. The vibrational spectra were interpreted with the aid of normal coordinate analysis based on scaled quantum mechanical force field. The results of the calculations were applied to simulated infrared and Raman spectra of the title compound, which showed excellent agreement with the observed spectra.

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Introduction

Hexafluorobenzene used in the manufacture of azo dyes, fungicides, rubber chemicals and explosives, and as an algicide in coolant water of air conditioning systems. It is an biological importance exhibiting compound used in tumor studies. So the vibration studies of these molecules would be helpful in understanding the various types of bonding and normal modes of vibration involved in this system. The modern vibrational spectrometry has proven to be an exceptionally powerful technique for solving many chemistry problems. It has been extensively employed both in the study of chemical kinetics and chemical analysis. The problem of signal assignment however, as well as understanding the relationship between the observed spectral features and molecular structure, and reactivity can be difficult. Even identification of fundamental vibrational wavenumbers often generates controversy.

Harmonic force fields derived from quantum mechanics are widely used for the calculation of wavenumbers and the modes of normal vibrations. Indeed, applying current quantum mechanical methods have opened up the way for calculating the wavenumbers and intensities of spectral bands with a minimum degree of arbitrariness (although the degree depends on the level of the quantum-mechanical treatment) and finding rational explanation for a number of chemical and physical properties of substances.[1-5]

However, for a proper understanding of IR and Raman spectra, a reliable assignment of all vibrational bands is essential. Recently, computational methods based on density functional theory are becoming widely used. These methods predict relatively accurate molecular structure and vibrational spectra with moderate computational effort. In particular, for polyatomic molecules the DFT methods lead to the prediction of more accurate molecular structure and vibrational wavenumbers than the conventional ab initio restricted Hartree-Fock (RHF) and Moller-plesset second order perturbation theory (MP2)

calculation to understand the structures and the fundamental vibrational wavenumbers. In this work DFT calculations are carried out to present a full description of the vibrational spectra of Hexafluorobenzene, especially the assignment of the vibrational modes, using B3LYP/6-31G**, to obtain the geometrics, vibrational wavenumbers, IR intensities and Raman activities.

Experimental details

The fine samples of HFB were obtained from Alfa Aesar company and were used as such for the spectral measurements. The Fourier transform infrared spectrum of the title compounds were recorded in the region 4000-400 cm⁻¹ using Perkin-Elmer spectrum RXI spectrophotometer equipped with He-Ne laser source, KBr beam splitter and LiTaO₃ detector. The samples were prepared by pressing HFB with KBr into pellet form. The FT Raman spectrum of HFB were recorded on a BRUCKER IFS-66V model interferometer equipped with an FRA-106 FT-Raman accessory in the stokes region 4000-100cm⁻¹ using 1064 nm line of a Nd: YAG laser for excitation operating at 200mW power. The reported wave numbers are believed to be accurate within ±1cm⁻¹.

Computational details

Quantum chemical density functional calculations were carried out with the 1998 version of the Gaussian suite of program[6] using the Becke3-Lee-Yang-Parr [B3LYP] functional[7-9] supplemented with the standard 6-31G** basis set (referred as DFT calculations). The Cartesian representation of the theoretical force constants has been computed at the fully optimized geometry by assuming C_s point group symmetry. The theoretical DFT force field was transformed from Cartesian into local internal coordinates and then scaled empirically according to the SQM procedure.[10-12]

$$F_{ij}^{Scaled} = (C_i C_j)^{\frac{1}{2}} F_{ij}^{B3LYP}$$

where C_i is the scale factor of coordinate i , F_{ij}^{B3LYP} is the B3LYP/6-31G* force constant in the local internal coordinates, and F_{ij}^{B3LYP} is the scaled force constant.

The transformation of force field from Cartesian to internal coordinate, the scaling,[13,14] the subsequent normal coordinate analysis, calculation of potential energy distribution (PED) and IR and Raman intensities were done on a PC with the version V7.0 of the Molvib program written by Sundius.[15,16] To achieve a close agreement between the observed and calculated wavenumbers, the least square fit refinement algorithm was used. The force field obtained by this way was then used to recalculate the normal modes PEDs and the corresponding theoretically expected IR and Raman intensities to predict the full IR and Raman spectra. For the plots of simulated IR and Raman spectra, pure Lorentzian band shapes were used with a bandwidth (FWHM) of 10cm^{-1} .

The prediction of Raman intensities was carried out by following the procedure outlined below. The Raman activities (S_i) calculated by the Gaussian 98 program and adjusted during the scaling procedure with Molvib were converted to relative Raman intensities (I_i) using the following relationship derived from the basic theory of Raman scattering.[17,18]

$$I_i = \frac{f(\nu_o - \nu_i)^4 S_i}{\nu_i \left[1 - \exp\left(\frac{-hc\nu_i}{KT}\right) \right]}$$

where ν_o is the exciting wavenumber (in cm^{-1} units), ν_i is the vibrational wave number of the i^{th} normal mode, h , c and k are the universal constants, and f is the suitably chosen common scaling factor for all peak intensities.

Results and discussion

Molecular geometry and Theoretical spectrum simulation

The optimized molecular structure of HFB was shown in Fig.1. The global minimum energy obtained by the DFT structure optimization was presented in Table 1. The optimized geometrical parameters obtained by the large (6-311+G**) basis set calculation were presented in Table 2.



Fig. 1. The optimized molecular structure of Hexafluorobenzene
Table 1. Total energies of Hexafluorobenzene, calculated at DFT (B3LYP)/6-31G* and (B3LYP)/6-311+G level**

Method	Energies (Hartrees)
6-31G*	-827.185639
6-311+G**	-827.596977

The optimized geometrical parameters calculated at B3LYP/6-311+G(d,p) level are slightly larger than those calculated at B3LYP/6-31G(d) level and these calculated values are well comparable with the available X-ray data on the whole[32]. It is listed Table 3. The title compound belongs to C_{3h} point group symmetry and their 30 normal modes are distributed between two symmetry species as, $\Gamma_{3N-6} = 21 A'$ (in-plane) + 9 A'' (out-of-plane). Detailed description of vibrational modes can be given by means of normal coordinate analysis (NCA). For this purpose, the full set of 42 standard internal coordinates containing 12 redundancies were defined as given in Table 4.

Table 2. Optimized geometrical parameters of Hexafluorobenzene obtained by B3LYP/ 6-311+G density functional calculations**

Bond length	Value(Å)	Bond angle	Value(Å)	Dihedral angle	Value(Å)
C2-C1	1.393715	C3-C2-C1	120.008682	C4-C3-C2-C1	-0.055960
C3-C2	1.393671	C4-C3-C2	119.984347	C5-C4-C3-C2	0.031983
C4-C3	1.393786	C5-C4-C3	120.002683	C6-C1-C2-C3	0.033994
C5-C4	1.393630	C6-C1-C2	120.007819	F7-C1-C6-C5	-
C6-C1	1.393638	F7-C1-C6	120.025583	F8-C2-C1-C6	179.95800
F7-C1	1.335638	F8-C2-C1	119.979388	F9-C3-C2-C1	179.98298
F8-C2	1.335633	F9-C3-C2	119.999072	F10-C4-C3-C2	-
F9-C3	1.335698	F10-C4-C3	120.019694	F11-C5-C4-C3	179.97600
F10-C4	1.335649	F11-C5-C4	119.985964	F12-C6-C1-C2	179.99004
F11-C5	1.335624	F12-C6-C1	120.025892		-
F12-C6	1.335700				180.00000

*for numbering of atom refer Fig. 1

Table 3. Optimized geometrical and experimental parameters of Hexafluorobenzene

Bond length	Value (Å)	
	Exp ^a	B3LYP ^b
C2-C1	1.39	1.393715
C3-C2	1.39	1.393671
C4-C3	1.39	1.393786
C5-C4	1.39	1.393630
C6-C1	1.39	1.393638
F7-C1	1.33	1.335638
F8-C2	1.33	1.335633
F9-C3	1.33	1.335698
F10-C4	1.33	1.335649
F11-C5	1.33	1.335624
F12-C6	1.33	1.335700

^aX-ray

^bThis work

Table 4. Definition of internal coordinates of Hexafluorobenzene

No(i)	symbol	Type	Definition
Stretching			
1 - 6	r_i	C-F	C1-F7,C2-F8,C3-F9,C4-F10,C5-F11,C6-F12
7 - 12	R_i	C-C	C1-C2,C2-C3,C3-C4,C4-C5,C5-C6,C6-C1
Bending			
13 - 24	β_i	C-C-F	C6-C1-F7,C2-C1-F7,C1-C2-F8,C3-C2-F8,C2-C3-F9,C4-C3-F9,C3-C4-F10,C5-C4-F10,C4-C5-F11,C6-C5-F11,C5-C6-F12,C1-C6-F12
25 - 30	α_i	Bring	C1-C2-C3, C2-C3-C4,C3-C4-C5,C4-C5-C6,C5-C6-C1,C6-C1-C2
Out-of-plane bending			
31 - 36	ω_i	ω C-F	F7-C1-C2-C6,F8-C2-C3-C1,F9-C3-C2-C4,F10-C4-C3-C5,F11-C5-C4-C6,F12-C6-C5-C1
Torsion			
37 - 42	τ_i	Tring	C1-C2-C3-C4,C2-C3-C4-C5,C3-C4-C5-C6,C4-C5-C6-C1,C5-C6-C1-C2,C6-C1-C2-C3

*for numbering of atom refer Fig. 1

From these, a non-redundant set of local symmetry coordinates were constructed by suitable linear combinations of internal coordinates following the recommendations of Fogarasi et. al [16, 17] are summarized in Table 5. The theoretically calculated DFT force fields were transformed in this later set of vibrational coordinates and used in all subsequent calculations.

Table 5. Definition of local symmetry coordinates and the value corresponding scale factors used to correct the force fields for Hexafluorobenzene

No.(i)	Symbol ^a	Definition ^b
1 - 6	C-F	r ₁ ,r ₂ ,r ₃ ,r ₄ ,r ₅ ,r ₆
7 - 12	C-C	R ₇ ,R ₈ ,R ₉ ,R ₁₀ ,R ₁₁ ,R ₁₂
13 - 18	C-C-F	(β ₁₃ -β ₁₄)/√2,(β ₁₅ -β ₁₆)/√2,(β ₁₇ -β ₁₈)/√2 (β ₁₉ -β ₂₀)/√2,(β ₂₁ -β ₂₂)/√2,(β ₂₃ -β ₂₄)/√2
19	Bring	(α ₂₅ -α ₂₆ +α ₂₇ -α ₂₈ +α ₂₉ -α ₃₀)/√6
20	Bring	(2α ₂₅ -α ₂₆ -α ₂₇ +2α ₂₈ -α ₂₉ -α ₃₀)/√12
21	Bring	(α ₂₆ -α ₂₇ +α ₂₈ -α ₂₉)/2
22 - 27	ωC-F	ω ₃₁ , ω ₃₂ , ω ₃₃ , ω ₃₄ , ω ₃₅ , ω ₃₆
28	Tring	(τ ₃₇ -τ ₃₈ +τ ₃₉ -τ ₄₀ +τ ₄₁ -τ ₄₂)/√6
29	Tring	(τ ₃₇ -τ ₃₉ +τ ₄₀ -τ ₄₂)/2
30	Tring	(-τ ₃₇ +2τ ₃₈ -τ ₃₉ -τ ₄₀ +2τ ₄₁ -τ ₄₂)/√12

^a These symbols are used for description of the normal modes by TED in Table 5.

^b The internal coordinates used here are defined in Table 3.

The global minimum energy obtained by the DFT structure optimization for HFB are calculated as -827.596977 KJ/mol. Fluorine is highly electronegative and wishes to obtain additional electron density. The calculated significant alteration of C-C bond lengths is good agreement with experimental structure of HFB. For visual comparison, the observed and simulated FT-IR and FT-Raman spectra of HFB are presented in Fig. 2 & Fig. 3.

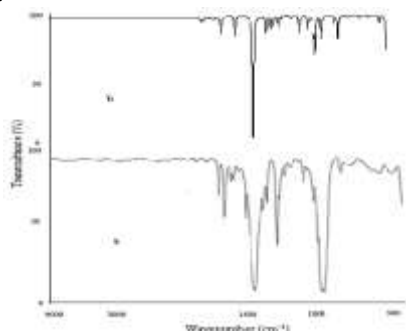


Fig. 2 FT-IR spectra of Hexafluorobenzene.
(a) Observed (b) Calculated with B3LYP/6-311+G**

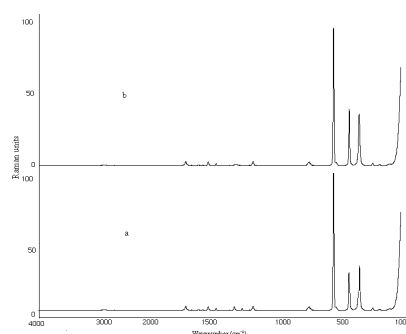


Fig. 3 FT-Raman spectra of Hexafluorobenzene.
(a) Observed (b) Calculated with B3LYP/6-311+G**

Vibrational force constant

The output files of the quantum-mechanical calculations contain the force constant matrix in Cartesian coordinates and in Hartree/Bohr² units. These force constants were transformed to the force fields in the internal local-symmetry coordinates. The local-symmetry coordinates, defined in terms of the internal valence coordinates following the IUPAC recommendations [23-25] are given in Table 5 for HFB. The force fields determined were used to calculate the vibrational potential energy distribution (PED) among the normal coordinates and listed in Table 6.

The bonding properties of HFB were influenced by the rearrangements of electrons during substitutions and addition reactions. The values of the stretching force constants between

carbon atoms in HFB are found to be higher. As the atom bonded to carbon increases in mass, the factor μ increases and consequently the wavenumbers decreases, since fluorine atoms are more electronegative and hence the bonded electrons between the carbon atoms are slightly shifted towards the halogen atoms of the title compounds. The values of the stretching force constants between carbon and fluorine atoms of HFB were found to be higher than the values of stretching force constant between carbon and hydrogen atoms.

SQM analysis and assignments

The unscaled wavenumbers obtained by B3LYP method are larger than the experimental values of HFB. In order to reproduce the calculated wavenumbers close to the observed wavenumbers, a selective scaling procedure was employed. The calculated wavenumbers were scaled using a set of transferable scale factors recommended by Rauhut and Pulay[14]. The SQM treatment improved the agreement between the experimental and the scaled wavenumbers for the title compound. The calculated vibrational wavenumbers of HFB are listed in Table 6 with the RMS deviations from experimental wavenumbers. Clearly the best agreement with experiment is achieved when the theoretical force field is scaled.

C C vibrations

There are six equivalent C C bonds in HFB and consequently there will be six C C stretching vibrations. In addition, there are several in-plane and out-of-plane bending vibrations of the ring carbons. However, due to high symmetry of HFB, many modes of vibrations are infrared inactive. In general the bands around 1400 to 1700cm⁻¹ in HFB derivatives are assigned to skeletal stretching C C bands. The bands observed at 1334,1577, 1683 and 1690cm⁻¹ of HFB are identified as C C stretching vibrations. The theoretically scaled C C stretching vibrations by B3LYP/6-311++G(d,p) are at 1326, 1564,1686 and 1687cm⁻¹ shows excellent agreement with recorded spectral data. The C C aromatic stretch, known as semicircle stretching, predicted at 1563cm⁻¹ is also in excellent agreement with experimental observations of 1560cm⁻¹ in FT-Raman spectra. As the energies of these vibrations are very close, there is an appreciable interaction between these vibrations and consequently their energies will be modified. The ring breathing and trigonal bending modes of HFB are assigned at 1013cm⁻¹. The theoretically computed values at 1016cm⁻¹ by B3LYP/6-311++G(d,p) method coincides with experimental observations. The theoretically calculated C C C out-of-plane and in-plane bending modes have been found to be consistent with the recorded spectral values.

C F vibrations

The vibrations belonging to the bond between the ring and the halogen atoms are worth to discuss here, since mixing of vibrations are possible due to the lowering of the molecular symmetry and the presence of heavy atoms on the periphery of molecule. Mooney assigned vibrations of C X group (X =F,Cl, Br, I) in the frequency range of 1129-480 cm⁻¹. Compounds with more than one fluorine atom exhibit very strong bands due to asymmetric and symmetric stretching mode. In FT-Raman spectrum of HFB the very strong band at 780 cm⁻¹ is assigned to C F stretching vibration. The theoretical wavenumber of C F stretching vibration coupled with C C C in-plane bending vibration 781 cm⁻¹ coincides very well with the experimental C F value. The C F inplane bending and out-of-plane bending vibrations are assigned to the Raman bands at 369 and 259 cm⁻¹, respectively. This is in agreement with the literature data[20-25].

Table 6. Detailed assignments of fundamental vibrations of Hexafluorobenzene by normal mode analysis based on SQM force field calculation

No.	Symmetry species Cs	Observed frequency (cm ⁻¹)		Calculated frequency (cm ⁻¹) with B3LYP/6-311+G** force field				TED (%) among type of internal coordinates ^c
		Infrared	Raman	Unscaled	Scaled	IR ^a A ₁	Raman ^b I ₁	
1	A'	1690	1688	1701	1687	0.000	7.472	CC(68),bring(13),CF(11),bCF(8)
2	A'	1683		1700	1686	0.001	7.472	CC(68),bring(13),CF(11),bCF(8)
3	A'	1577		1577	1564	331.454	0.000	CC(50),CF(39),bCF(12)
4	A'		1560	1576	1563	331.763	0.000	CC(50),CF(39),bCF(12)
5	A'	1527		1542	1530	0.000	1.472	CF(65),CC(35)
6	A'	1364	1350	1370	1359	0.000	0.000	CF(62),bring(38)
7	A'	1334		1337	1326	0.000	0.000	CC(96)
8	A'		1190	1201	1191	0.000	1.195	CF(79),CC(11),bring(10)
9	A'	1159		1201	1150	0.000	1.194	CF(79),CC(11),bring(10)
10	A'	1022		1032	1024	221.325	0.000	CF(65),bCF(19),CC(16)
11	A'	1013		1028	1016	221.316	0.000	CF(65),bCF(19),CC(16)
12	A'	795		826	781	0.000	0.000	bCF(100)
13	A''		755	769	750	0.000	0.000	gCF(51),tring(49)
14	A''			612	605	0.000	0.000	gCF(67),tring(33)
15	A'	587		627	593	0.000	0.000	bring(67),CF(33)
16	A'		580	600	567	0.000	25.681	CC(66),CF(34)
17	A''	529		551	521	0.000	0.000	tring(59),gCF(41)
18	A'	445		469	444	0.000	5.046	bring(74),CC(10),CF(8),bCF(8)
19	A'		484	469	444	0.000	5.047	bring(74),CC(10),CF(8),bCF(8)
20	A''			390	379	0.000	2.808	gCF(100)
21	A''		370		369	0.000	2.808	gCF(100)
22	A'			329	311	1.266	0.000	bCF(72),CC(25)
23	A'		310	328	310	1.268	0.000	bCF(72),CC(25)
24	A'			280	265	0.000	0.000	bCF(99)
25	A'		259	274	259	0.000	0.212	bCF(76),bring(23)
26	A'			273	258	0.000	0.211	bCF(76),bring(23)
27	A''		214	226	214	4.971	0.000	gCF(100)
28	A''		184	194	184	0.000	0.000	tring(100)
29	A''			145	137	0.000	0.000	tring(100)
30	A''		137		135	0.000	0.000	tring(100)

Conclusion

In this work, the SQM force field method based on DFT calculations at the B3LYP/6-311+G** level have been carried out to analyze the vibrational frequencies of HFB. The various modes of vibrations were unambiguously assigned based on the results of the TED output obtained from normal coordinate analysis. There is a fairly good correlation between the experimental vibrational frequencies and the calculated of harmonic ones. This theoretical information was useful in the assignment of the different fundamentals.

Acknowledgement

The authors are thankful to the Sophisticated Analytical Instrumentation Facility (SAIF), IIT Madras, Chennai, for spectral measurements. Help rendered by R.Kokila, Spectroscopic Division, Photonics Research Foundation, Salem, in the calculation part highly acknowledged.

References

- [1]Jain MK, Sharma SC, Organic Chemistry, Shoban Lal Nagin Chand & Co., Educational Publishers, Delhi.1980.
- [2]Wilson EB, Decius JC, Cross PC. Molecular Vibrations: The Theory of Infrared and Raman Vibrational Spectra, McGraw Hill, New York, 1955.
- [3]Volkenstein MV, Elyashevitch MA, Stepanov BI. Kolebaniya Molecule (Molecular vibrations) Vols and II GITTL, Moscow, 1949 (in Russian).
- [4]Cyvin SJ. Molecular Vibrations and Mean Square Amplitudes, Elsevier, Amsterdam, 1968.
- [5]Gribov LA, Orville-Thomas MJ. Theory and Methods of Calculation of Molecular Spectra, Wiley, Chochester, 1988.
- [6]M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheesman, V.G. Zakrzewski, J.A. Montgomery,

- R.E. Stratmann, Jr., J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V.Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, N. Rega, P. Salvador, JJ. Dannenberg, D.K. Malich, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stetanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Jumpers, R.L. Martin, D.J. Fox, T. Keith, M.A. AL-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian 98, Revision A. Vol. 11.4, Gaussian Inc., Pittsburgh, PA, 2002.
- [7]Lee C, Yang W, Parr RG. Phys. Rev., 1998; B37: 785.
- [8]Becke AD, J. Chem.Phys. 1993; 98: 5648.
- [9]Pulay P, Forgarasi G, Pang F, Boggs JE. J. Am. Chem. Soc. 1979; 101: 2550.
- [10]Pulay P, Forgarasi G, Pongor G, Boggs JE, Vargha A. J. Am. Chem. Soc. 1983; 105: 7037.
- [11]Forgarasi G, Pulay P, During JR. (Ed.), Vibrational Spectra and Structure, Elsevier, Amsterdam, 1985; 14: 125(Chapter 3).
- [12]Pulay P, Schaefer HF. Third Edition, Application of Electronic Structure Theory, Modern Theoretical Chemistry, Plenum, New York, 1997; 4; 153.
- [13]Forgarasi G, Zhou X, Taylor PW, Pulay P. J. Am. Chem. Soc. 1992; 114: 8191.
- [14]Rauhut G, Pulay P. J. Phys. Chem. 1995; 99: 3093.
- [15]Sundius T. MOLVIB a program for Harmonic Force Fields calculations, QCPE Program No. 604, J. Mol. Struct. 1990; 218: 321.
- [16]Sundius T. Vib. Spectrosc. 2002; 29: 89.

- [17] Keresztury G, Holly S, Varga J, Besenyei G, Wang AY, Durig JR. *Spectrochim. Acta Part A*. 1993; 49: 2007.
- [18] Keresztury G. Raman spectroscopy: Theory, in *Handbook of Vibrational Spectroscopy*, Chalmers JM, Griffiths PR (eds), John Wiley & Sons, Ltd., Asia. 2002; 1: 71.
- [19] G. Rauhut, P. Pulay, *J. Phys. Chem.* 99 (1995) 3093.
- [20] G. Keresztury, S. Holly, J. Varga, G. Besenyei, A.V. Wang, J.R. Durig, *Spectrochim. Acta* 49A (1993) 2007.
- [21] G. Keresztury, in: J.M. Chalmers and P.R. Griffiths (Eds), *Handbook of Vibrational Spectroscopy vol.1*, John Wiley & Sons Ltd. (2002), p. 71.
- [22] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [23] H.D. Cohen, C.C.J. Roothan, *J. Chem. Phys.* 435 (1965) S34.
- [24] D.N. Sathyanarayana, *Vibrational Spectroscopy—Theory and Applications*, second ed., New Age International (P) Limited Publishers, New Delhi, 2004.
- [25] George Socrates, *Infrared and Raman Characteristic Group Frequencies - Tables and Charts* (third ed.), John Wiley & Sons, Chichester (2001).