Vol. **112** (2007) *ACTA PHYSICA POLONICA A* Supplement

Structure and Vibrational Spectra of 1,3,5-Trimethoxybenzene

A. Pawlukojć[a], G. Bator[b] and L. Sobczyk[b]

[a]Joint Institute for Nuclear Research, 141980 Dubna, Russia
and
Institute of Nuclear Chemistry and Technology
Dorodna 16, 03-195 Warsaw, Poland
[b]Faculty of Chemistry, University of Wrocław
F. Joliot-Curie 14, 50-383 Wrocław, Poland

Dedicated to the memory of Professor J. Prochorow

Inelastic neutron scattering infrared and Raman spectra of the crystalline 1,3,5-trimethoxybenzene were measured and compared with simulated ones by using the Gaussian 98 and DMol3 programs at density functional theory methods. Application of the double numerical plus polarization basis set for the crystalline state within the local density Perdew and Wang (PWC functionals) approximation quite well reproduces the low frequency bands related to the methyl group librational modes, which are very sensitive to molecular interactions. Infrared spectra for the crystalline sample and CCl_4 solution show spectacularly the change of low frequency modes by going from the symmetric D_{3h} molecules in the gas phase to asymmetric ones in the crystal.

PACS numbers: 78.30.–j, 78.70.Nx, 61.66.Hq

1. Introduction

We have been interested in searching for compounds containing methyl groups being a probe for intermolecular interactions reflected in low frequency vibrational modes. 1,3,5-trimethoxybenzene was selected as one of such compounds. It forms relatively stable charge-transfer (CT) complexes with electron acceptors, such like tetracyanoethylene, as shown in Refs. [1–3].

It seemed justified to study the dynamics of methyl groups from the point of view of the rotational potential. There is only limited information related to the compounds containing methoxy groups. This relates to the methoxy group

rotation in anisole [4], relationships between the C–O bond length and the methoxy group rotational potentials [5] and *ab initio* calculations for anisole [6]. There are several other communications connected with the methoxy groups but in rather very complicated molecular structures. As follows from the review [7] and the survey of literature performed by us the methoxy aromatic derivatives have not been investigated by using spectroscopic vibrational techniques.

1,3,5-trimethoxybenzene merits, independently, to be carefully investigated because of its interesting physical properties related to the structure. As follows from structural [8–10] and NMR studies [9, 11] the molecules of 1,3,5--trimethoxybenzene lose the D_{3h} symmetry and one of the OCH_3 groups is twisted in opposite to remaining groups direction and deflected from the ring plane. This leads to an inequivalence of CH_{ar} groups well reflected in the ^{13}C NMR spectrum in the solid state. The calculations concerning the conformation of the free molecules show full equivalence of all three groups.

The Cc space group of crystalline 1,3,5-trimethoxybenzene prompted a group of authors [12] to analyse this compound as a candidate of organic ferroelectrics. This was also a reason to undertake detailed studies of the dynamics by using complementary spectroscopic methods: inelastic neutron scattering (INS), infrared, and Raman.

2. Experimental and calculations

1,3,5-trimethoxybenzene was purchased from Aldrich and used without any additional treatments.

Neutron scattering data were collected at the pulsed IBR-2 reactor in Joint Institute for Nuclear Research in Dubna (Russia) using the time-of-flight inverted geometry spectrometer NERA-PR [13]. The temperature maintained at the sample was 20 K. The spectrum was converted from neutrons per channel to $S(Q,\omega)$ scattering function per energy transfer. At the energy transfer between 5 and 100 meV the relative INS resolution was estimated to be *ca.* 3%.

The IR spectra were recorded at room temperature in Nujol or Fluorube suspension using CsI windows on a FT-IR Bruker IFS66 Spectrometer with a resolution of 1 cm^{-1}. The spectra of CCl_4 solutions were also recorded.

Powder Raman spectra were measured at room temperature with Raman or U-1000 Jobin-Yvon spectrometer, equipped with CCD and photomultiplier detectors. The 515.5 nm line (power of *ca.* 200 mW at a sample) of the Ar^+ laser was used as an exciting radiation.

The total energy optimisation and the harmonic force field calculations have been performed using density functional theory (DFT) method. According to the Hohenberg–Kohn theory [14], which states that all ground-state properties are functionals of the charge density ρ, the total energy $E_v(\rho)$ is equal to

$$E_v(\rho) = T_s(\rho) + V_{ne}(\rho) + J_{ee}(\rho) + E_{xc}(\rho), \tag{1}$$

where $T_s(\rho)$ is a kinetic energy of the system of independent electrons, $V_{ne}(\rho)$ de-

scribes the potential energy of the nuclear–electron attraction and nuclear–nuclear repulsion, $J_{\mathrm{ee}}(\rho)$ is the electron–electron repulsion term (Coulomb self-interaction of the electron density) and $E_{\mathrm{xc}}(\rho)$ is the exchange-correlation term including the remaining part of the electron–electron interactions. The Kohn–Sham equation [15] of the Hohenberg–Kohn density functional theory may be written as

$$\left[-\frac{\hbar^2\nabla^2}{2m} + v_{\mathrm{ext}}(\boldsymbol{r}) + v_{\mathrm{H}}(\boldsymbol{r}) + v_{\mathrm{xc}}(\boldsymbol{r})\right]\varphi_{k,\sigma}(\boldsymbol{r}) = \varepsilon_{k,\sigma}\varphi_{k,\sigma}(\boldsymbol{r}). \tag{2}$$

Here, $v_{\mathrm{ext}}(\boldsymbol{r})$ is the external Coulomb potential of nuclei, $v_{\mathrm{H}}(\boldsymbol{r})$ is the Hartree potential resulting from the electron density

$$\rho(r) = \sum_{\sigma=\uparrow,\downarrow}\sum_{k}^{\mathrm{occ}} \left|\varphi_{k,\sigma}(r)\right|^2. \tag{3}$$

Residual many-electron effects on the density are included via the exchange--correlation potential or functional derivative

$$v_{\mathrm{xc}}(r) = \frac{\delta E_{\mathrm{xc}}(\rho)}{\delta\rho(r)}, \tag{4}$$

where the exchange-correlation energy E_{xc} is a universal but unknown functional of the density $\rho(\boldsymbol{r})$.

For the crystalline compound the calculations have been performed by using of the DMol3 program [16, 17], as a part of Materials Studio package [18], for the local density approximation (LDA) at $E_{\mathrm{xc}}^{\mathrm{LDA}}(\rho)$ functional described by Perdew and Wang [19] (PWC functional) and double numerical plus polarization (DNP) basis set as implemented in DMol3. The B3LYP/6-31G** (Becke's three parameter hybrid functional using the LYP correlation functional [20]) calculations tending towards the optimised structure of the molecule and its internal frequencies were performed by using Gaussian 98 program [21] for both isolated molecules and that in crystalline state.

To make a proper assignment the potential energy distribution (PED) for normal modes was calculated using the GAMESS program [22]. The corresponding modes were defined by means of internal coordinates according to [23].

INS spectra were reproduced based on calculated mass weighted normal vibrational coordinates using auntieCLIMAX program [24] adapted to parameters of the NERA-PR spectrometer.

3. Results and discussion

3.1. Structure

X-ray diffraction and calculated for the isolated state structures of the 1,3,5--trimethoxybenzene molecules with atom numbering are presented in Fig. 1. The packing of molecules in the lattice are shown in Fig. 2 as a projection of the unit cell along the *b*-axis. The experimental data are related to the diffraction experiments at 115 K [25]. The main selected bond lengths and angles as well as torsion angles are collected in Tables I–III.

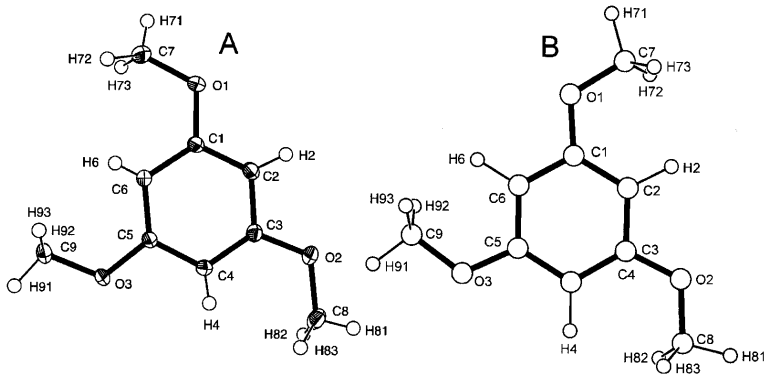

Fig. 1. The structure of 1,3,5-trimethoxybenzene molecules: (A) X-ray experimental [25] with atom numbering; (B) calculated for the isolated molecules in the gas phase.

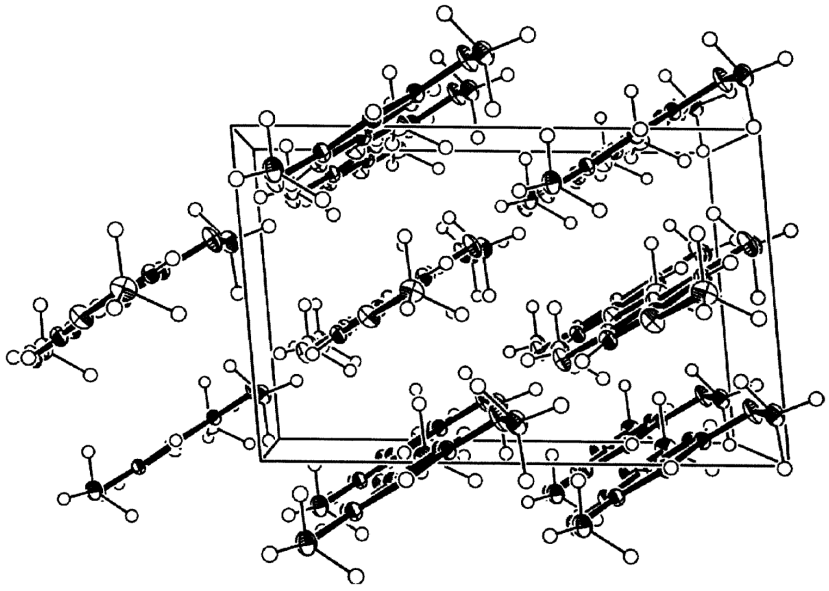

Fig. 2. The packing of 1,3,5-trimethoxybenzene molecules represented by the projection along the *b*-axis.

From the comparisons it follows that calculated structural parameters both for isolated molecules and for the one in the crystalline lattice are close to the experimental values. Nevertheless, the parameters obtained by using the PWC(dnp) approach are markedly closer to the experimental ones. However, the comparison of torsional angles, which describe the turning of the methoxy groups and some deviation from the planarity, is of particular importance.

TABLE I

Experimental and calculated bonds lengths for 1,3,5-trimethoxybenzene [Å].

Coordinates	Experimental	Calculated	
	[25]	B3LYP/6-31G**	PWC(dnp)
C1–C2	1.385	1.393	1.389
C2–C3	1.394	1.399	1.394
C3–C4	1.391	1.397	1.391
C4–C5	1.397	1.401	1.396
C5–C6	1.390	1.399	1.392
C6–C1	1.398	1.405	1.398
C1–O1	1.369	1.367	1.356
C3–O2	1.365	1.365	1.354
C5–O3	1.367	1.367	1.353
O1–C7	1.427	1.417	1.413
O2–C8	1.434	1.419	1.414
O3–C9	1.432	1.417	1.415
R^2		0.9009	0.8899

TABLE II

Experimental and calculated bonds angles for 1,3,5-trimethoxybenzene [°].

Coordinates	Experimental	Calculated	
	[25]	B3LYP/6-31G**	PWC(dnp)
C1–C2–C3	118.8	119.3	119.1
C2–C3–C4	121.4	120.9	121.1
C3–C4–C5	118.0	118.8	118.5
C4–C5–C6	122.4	121.6	121.7
C5–C6–C1	117.5	118.3	118.3
C6–C1–C2	121.9	121.2	121.3
C6–C1–O1	123.2	123.4	122.8
C2–C1–O1	115.0	115.4	115.9
C1–O1–C7	117.6	118.6	117.2
C2–C3–O2	115.1	115.3	115.8
C4–C3–O2	123.6	123.8	123.0
C3–O2–C8	117.4	118.3	117.3
C4–C5–O3	114.4	114.7	115.2
C6–C5–O3	123.2	123.7	123.1
C5–O3–C9	118.3	118.5	118.2
R^2		0.9728	0.9858

TABLE III

Experimental and calculated torsion angles for 1,3,5-trimethoxybenzene [°].

Coordinates	Experimental	Calculated	
	[25]	B3LYP/6-31G**	PWC(dnp)
C1–C2–C3–C4	–0.67	0.00	0.00
C2–C3–C4–C5	–1.10	0.00	–1.32
C3–C4–C5–C6	1.73	0.00	1.41
C4–C5–C6–C1	–0.54	0.00	–0.19
C5–C6–C1–C2	–1.34	0.00	–1.19
C6–C1–C2–C3	1.94	0.00	1.28
C6–C1–O1–C7	–2.37	0.00	0.77
C2–C1–O1–C7	177.93	180.00	–179.30
C2–C3–O2–C8	177.91	–180.00	–177.8 0
C4–C3–O2–C8	–1.74	0.00	3.66
C4–C5–O3–C9	171.70	–180.00	169.48
C6–C5–O3–C9	–7.99	0.00	–9.71

3.2. Vibrational spectra

The calculated and experimental frequencies of the internal modes in the range up to 1600 cm^{-1} for the solid state are presented in Table IV, while comparison of the INS spectra in the region up to 800 cm^{-1}, together with simulated ones by using the auntieCLIMAX program is shown in Fig. 3.

It seems justified to emphasize that calculated frequencies for the solid state by using the PWC(dnp) method are close to experimental ones. This means that in the applied method the molecular interactions via CH_3 groups are reflected quite well. In the case of the B3LYP functionals used for the isolated molecules the deviations are very large: the larger the lower are frequencies. It seems that such a situation is typical of modes, into which the liberational motion of methyl groups is involved [26].

To characterise the effect of the conformation on the IR spectra we decided to compare the spectra recorded for CCl_4 solution, where we have to expect conformation of free molecules, with those for the solid state. The comparison is presented in Fig. 4 in the low frequency region where the effect of the conformation should be pronounced. As it can be seen, two bands above 500 cm^{-1}, at 538, and 592 cm^{-1} (ring deformation), do not change their positions going from the solid state to the solution. Three bands, at 132 cm^{-1} (OCH_3 wagg.), 203 cm^{-1} (CH_3 tors.) and 445 cm^{-1} (COC bend), are markedly shifted toward the lower frequencies. Two bands, at 319 cm^{-1} (COC bend) and 484 cm^{-1} (ring def.), observed in the solid state spectra do not appear in the solution ones due to the selection rules (transition to higher symmetry).

TABLE IV

Calculated and experimental frequencies for 1,3,5-trimethoxybenzene[a].

Approximate assignments[b]	Calculated		Experiment		
	B3LYP/6-31G**	PWC(dnp)	INS	IR	Raman
Lattice modes		20-90, 21 modes	Massive up to 90		83, 91
O–$CH_{3\,\mathrm{wagg.}}$	65	118	132	132	127
O–$CH_{3\,\mathrm{wagg.}}$	75	133	145		
O–$CH_{3\,\mathrm{wagg.}}$	101	147	155		
C–$O_{\mathrm{bend.}}$	168	185	194		192
Ring tors.	181	199	214	203	
C–$O_{\mathrm{bend.}}$	188	215	220		
$CH_{3\,\mathrm{tors.}}$	201	226	232		
$CH_{3\,\mathrm{tors.}}$	223	254	255	244	244
$CH_{3\,\mathrm{tors.}}$	252	265	266		
Ring tors.	265	285	283		
Ring tors.	280	296	299		
C–O–$C_{\mathrm{bend.}}$	300	327	328	319	315
C–O–$C_{\mathrm{bend.}}$	354	371	370	368	366
C–O–$C_{\mathrm{bend.}}$	428	446	452	445	443
Ring def.	470	484	492	484	482
Ring def.	521	538	548	538	536
Ring def.	572	593	597	592	591
C–$O_{\mathrm{wagg.}}$	596	607	623	616	611
C–$O_{\mathrm{wagg.}}$	598	616	624	641	
C–$O_{\mathrm{bend.}}$	625	643	653	688	
C–$O_{\mathrm{wagg.}}$	660	682	699		
C–$H_{\mathrm{wagg.}}$	759	761	793	782	
C–$H_{\mathrm{wagg.}}$	781	800	821	824	
C–$H_{\mathrm{wagg.}}$	795	837	836	849	
C–$O_{\mathrm{str.}}$, O–$C_{\mathrm{str.}}$	910	934		916	914
C–$O_{\mathrm{str.}}$,O–$C_{\mathrm{str.}}$	934	963		943	
C–$C_{\mathrm{str.}}$	969	982		990	990
O–$C_{\mathrm{str.}}$	1041	1058		1035	1034
O–$C_{\mathrm{str.}}$	1049	1067		1063	1063
O–$C_{\mathrm{str.}}$	1061	1072		1069	
$CH_{3\,\mathrm{rock.}}$	1130	1120			
$CH_{3\,\mathrm{rock.}}$	1131	1123			
$CH_{3\,\mathrm{rock.}}$	1132	1129			
$CH_{3\,\mathrm{rock.}}$	1147	1144			

TABLE IV (cont.)

Calculated and experimental frequencies for 1,3,5-trimethoxybenzene[a].

Approximate assignments[b]	Calculated		Experiment		
	B3LYP/6-31G**	PWC(dnp)	INS	IR	Raman
Lattice modes		20-90, 21 modes	Massive up to 90		83, 91
$C–H_{bend.}$	1149	1152		1152	
$CH_{3\,rock.}$	1166	1165			
$CH_{3\,rock.}$	1180	1194		1196	1190
$C–H_{bend.}$	1192	1200		1207	1209
$C–H_{bend.}$	1236	1225		1250	
$C–C_{str.}$, $C–O_{str.}$	1317	1344		1323	1316
$C–C_{str.}$, $C–O_{str.}$	1338	1385		1338	1338
$CH_{3\,bend.\,sym.}$	1412	1392		1377	
$CH_{3\,bend.\,sym.}$	1422	1396			
$CH_{3\,bend.\,asym.}$	1442	1401		1401	
$CH_{3\,bend.\,sym.}$	1443	1405			
$CH_{3\,bend.\,asym.}$	1444	1409			
$CH_{3\,bend.\,asym.}$	1444	1416			
$CH_{3\,bend.\,asym.}$	1452	1424		1425	1427
$C–C_{str.}$, $C–O_{str.}$	1455	1432		1436	1447
$CH_{3\,bend.\,asym.}$	1459	1440			1453
$CH_{3\,bend.\,asym.}$	1464	1473		1458	
$C–O_{str.}$, $C–C_{str.}$	1471	1478		1479	1589
$C–C_{str.}$	1580	1603			1606
$C–C_{str.}$	1601	1622			

[a]B3LYP frequencies are scaled by SF = 0.96; [b]abbreviations used: wagg. — wagging, tors. — torsional, ring def. — ring deformation, str. — stretching, rock — rocking, bend sym. — bending symmetric, bend asym. — bending asymmetric.

4. Conclusions

The application of complementary vibrational spectroscopic methods, i.e. INS, Raman scattering, and IR absorption combined with theoretical methods of simulation of the structure and spectra in the gas and solid states, allowed us to perform a detailed discussion of a behaviour of the 1,3,5-trimethoxybenzene molecules. From the studies accomplished in this paper the advantages of the INS method were convincingly shown, which yielded precise information on the low frequency modes connected with the deformation motions of the methoxy groups, which were particularly sensitive to intermolecular interactions.

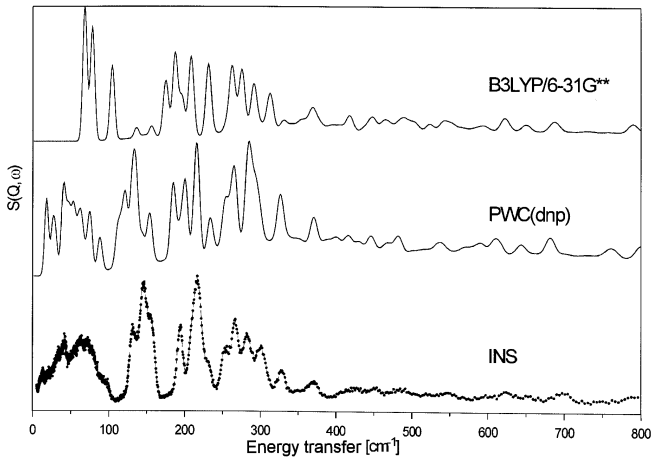

Fig. 3. INS spectra of 1,3,5-trimethoxybenzene compared with simulated ones by using the PWC(dnp) method for the crystalline state and simulated by using B3LYP/6-31G(dp) method applied to isolated molecules in conformation taking place in the crystal.

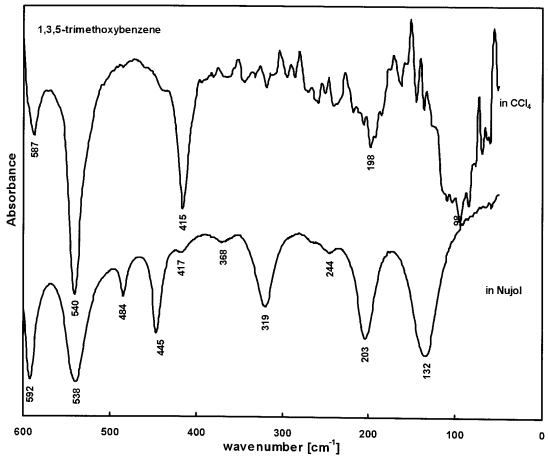

Fig. 4. Comparison of infrared spectra recorded for powder sample and for solution in CCl_4 of 1,3,5-trimethoxybenzene.

In the present paper we have shown that the application of theoretical methods accessible within the DMol3 programme to the solid state allowed us for a satisfactory reproduction of the INS spectra. In the case of theoretical methods applied for the gas phase a drastic difference between the calculated and experimental frequencies took place. The applied program reproduced also very well the structure and conformation of 1,3,5-trimethoxybenzene in the crystalline state. The conformation was not the same in this phase that was spectacularly reflected in the IR spectra measured in the crystalline state and in the CCl_4 solution.

The results obtained in this paper with respect to the low frequency modes can be used in further investigations of the non-conventional C–H$\cdots$Y hydrogen bonds, which are mainly responsible for the increase in frequencies of the modes under consideration. There is an analogy to usual conventional hydrogen bonds, in which one observes a drastic increase in the bending vibration frequencies of the proton-donor groups, too.

Acknowledgments

The calculations were performed on computers of Wrocław Centre for Networking and Supercomputing, calculating grant no. 2006/5 and in Interdisciplinary Centre for Mathematical and Computational Modeling, Warsaw University, calculating grant no. G30-15.

MATERIALS STUDIO package was used under POLAND COUNTRY-WIDE LICENSE.

References

[1] A. Zweig, *J. Phys. Chem.* **67**, 506 (1963).

[2] A. Zweig, J.E. Lehnsen, A. Murray, *J. Am. Chem. Soc.* **85**, 3933 (1963).

[3] J.E. Frey, T. Alello, D.N. Beaman, S.D. Comba, Shi-liu Fu, J.J. Puckett, *J. Org. Chem.* **59**, 1817 (1994).

[4] M.A. Vincent, I.H. Hillier, *Chem. Phys.* **140**, 35 (1990).

[5] J. Klocker, A. Karpfen, P. Wolschann, *J. Mol. Struct. (Theochem)* **635**, 141 (2003).

[6] S. Tsuzuki, H. Houjou, Y. Nagawa, K. Hiratani, *J. Phys. Chem. A* **104**, 1332 (2000).

[7] M. Prager, A. Heidemann, *Chem. Rev.* **97**, 2933 (1997).

[8] T.R. Steger, E.O. Stejskal, R.A. McKay, B.R. Stults, J. Schaefer, *Tetrahedron Lett.* **4**, 295 (1979).

[9] S.T. Howard, T.M. Krygowski, M.L. Główka, *Tetrahedron* **52**, 11379 (1996).

[10] B. Ray Stults, *Cryst. Struct. Commun.* **8**, 401 (1979).

[11] C.M. Carter, J.C. Facelli, D.W. Aldeman, D.M. Grant, N.K. Dalley, B.E. Wilson, *J. Chem. Soc. Faraday Trans. 1* **84**, 3673 (1988).

[12] Z. Zikmund, P. Vanek, M. Havrankova, B. Brezina, M. Cermak, M. Vasa, *Ferroelectrics* **158**, 223 (1994).

[13] I. Natkaniec, S.I. Bragin, I. Brankowski, J. Mayer, in: *Proc. 13th Meeting of the Int. Collaboration on Advanced Neutron Sources, Abington*, RAL Report 94-025, Vol. I, Abington 1993, p. 89.

[14] P. Hohenberg, W. Kohn, *Phys. Rev.* **136**, B864 (1964).

[15] W. Kohn, L.J. Sham, *Phys. Rev.* **140**, A1133 (1965).

[16] B. Delley, *J. Chem. Phys.* **92**, 508 (1990).

[17] B. Delley, *J. Chem. Phys.* **113**, 7756 (2000).

[18] http://www.accelrys.com/.

[19] J.P. Perdew, Y. Wang, *Phys. Rev. B* **45**, 13244 (1992).

[20] A.D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).

[21] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Mongmery, R.E. Stratmann, 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. Peterson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al.-Laham, C.Y. Peng, A. Nanaayakkara, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Anders, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian-98, Revisions A-7, Gaussian Inc., Pittsburgh, PA 1998.

[22] M.W. Schmidt, K.K. Baldrige, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S.J. Su, T.L. Windus, M. Depois, J.A. Montgomery, *J. Comput.Chem.* **14**, 1347 (1993).

[23] P. Pulay, G. Forgasi, F. Pang, J.E. Boggs, *J. Am. Chem.* **101**, 2550 (1979).

[24] A.J. Ramirez-Cuesta, *Comput. Phys. Commun.* **157**, 226 (2004).

[25] M.L. Główka, private communication.

[26] A. Pawlukojć, L. Sobczyk, *Trends Appl. Spectr.* **5**, 117 (2004).