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REGULAR ARTICLE

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A self-consistent reaction field model of solvation using distributed multipoles. II: second energy derivatives and application to vibrational spectra

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Abstract The use of distributed multipoles in the formalism of the reaction field factors allowed us to develop a computational scheme adapted to quantum chemical computations on a molecule solvated by a dielectric continuum. The algorithm used to compute the second energy derivatives is developed and, after its implementation in a quantum chemical computational code, permits the computation of the vibrational frequencies of the solute. This approach has been tested successfully on two test molecules and applied to the study of the solvent effect on the structure and the vibrational spectrum of a series of parasubstituted benzonitriles.

Introduction

The availability of the second derivatives of energy with respect to atomic coordinates in quantum chemistry computational codes has made the simulation of vibrational spectra quite common [1], at least in the harmonic approximation which may be corrected thanks to the use of scaling factors [2]. The physical influence of a solvent on these spectra can be addressed as well as by means of the simple continuum models of solvation in which the solvent is represented by a dielectric continuum and the solute is assumed to fill a cavity created in the dielectric [3]. In addition, the possibility of having a reasonable estimate of the effect of the solvent on the Hessian components may be very useful to locate transition states and therefore to study solvent effects on chemical reactions [4]. Among the most widely used models, the Pisa Continuum Model (PCM) [5,6] or the COSMO model [7] are based on numerical integrations which may become the rate-determining process in computations. On the other hand models based on a multipole expansion of the solute's charge distribution widely make use of analytical formulae, but the exact results imply an infinite expansion which, in practice is truncated to a finite order. The error due to this truncation is often of the same order of magnitude as that introduced by the numerical integrations, but in the classical case of a one center multipole expansion, it may happen that the convergence is not satisfactory. These convergence problems disappear when one uses a distributed multipole expansion [8,9], in particular when this expansion is distributed on all the atoms of the solute. There is an infinite number of possible distributions which are mathematically equivalent [10]. In a previous paper we developed the method with three different distributions and we concluded that two of them were the most useful [11]. In the present paper we focus our attention on the computation of the Hessian of a molecule interacting with a continuum through the distributed expansions of the molecular electrostatic potential selected previously. An application to the solvent effect on some localized stretching vibrational frequencies of some organic molecules is presented in order to illustrate the possibilities of this approach.

Principles of the method

The charge distribution of the solute is assumed to be represented by a distribution of multipoles, $M_L(I)$ on a series of centers $I, J, \ldots$, here the atoms. The symbol L stands for the couple of indices (l, m) used to define a multipole component in the spherical tensor theory [12,13]

The sum of the energy of the solute and the solute–solvent free energy of interaction is expanded as:

$$E = \langle H_o \rangle_s - \frac{1}{2} \sum_L \sum_J \sum_K R_L(J, K) M_L(K) \qquad (1)$$

where $\langle H_o \rangle_s$ stands for the expectation value of the Hamiltonian of the solute computed with the wavefuction optimised in the solution, $R_L(J, K)$ denotes the component of the reaction potential acting on $M_L(K)$, created by the multipoles defined at center J. This quantity is defined by:

$$R_L(J, K) = \sum\nolimits_{L'} f_{L,L'}(J, K) M_{L'}(J) \qquad (2)$$

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In the present study we consider two distributions of multipoles defined in reference [11]. For the Gaussian averaged distribution (GAD), we use an algorithm which does not require the translation of the multipoles. In this algorithm a pair of atomic orbitals $|\mu\rangle$ and $|\nu\rangle$ contribute to the component $M_l^m(K)$at center K by quantity:

$$\frac{\langle\mu|\,\mathbf{M}_l^m(K)\,|\nu\rangle\, e^{-\overline{GK}^2}}{\sum_L e^{-\overline{GL}^2}} \tag{3}$$

where G denotes the centroid of orbitals $|\mu\rangle$ and $|\nu\rangle$ and the sum on L is extended to all the centers.

In the Mulliken Sokalski–Poirier distribution the m component of multipole of rank l in K is defined by:

$$M_l^m(K) = \sum\nolimits_{\mu\in K}\sum\nolimits_{\nu} P_{\mu\nu}\,\langle\mu|\,\mathbf{M}_l^m(K)\,|\nu\rangle \tag{4}$$

where the first sum is limited to the orbitals centered on atom K.

The second derivatives of E with respect to a couple of nuclear coordinates k and l take the form:

$$\begin{aligned}\frac{\partial^2 E}{\partial k\partial l} = {} & \frac{\partial^2\langle H_0\rangle}{\partial k\partial l} - \sum\nolimits_J\sum\nolimits_K\sum\nolimits_L R_L(J,K)\frac{\partial^2 M_L(K)}{\partial k\partial l} \\ & -\sum\nolimits_J\sum\nolimits_K\sum\nolimits_L\left\{\sum\nolimits_{L'}\frac{1}{2}\left[\frac{\partial M_L(J)}{\partial k} f_{L,L'}(J,K)\frac{\partial M_{L'}(K)}{\partial l}\right]\right. \\ & \left. +\left[\frac{\partial R_L(J,K)}{\partial k}\right]_M\frac{\partial M_L(K)}{\partial l}\right\} \\ & -\frac{1}{2}\sum\nolimits_J\sum\nolimits_K\sum\nolimits_L\left[\frac{\partial^2 R_L(J,K)}{\partial k\partial l}\right]_M M_L(K)\end{aligned} \tag{5}$$

The first derivatives which appear in this equation have been computed in the previous paper [11], the second derivatives of $\langle H_o\rangle_s$ is computed in the standard codes and the second derivatives of the moments are straightforward is one refers to their definitions. The quantities

$$\left[\frac{\partial^2 R_L(J,K)}{\partial k\partial l}\right]_M$$

are the second derivatives of the reaction field components when the moments are constant [11]. They are computed by a procedure similar to that developed for the first derivatives.

The components of the reaction field appear in the boundary conditions for the electric potential and the field at the surface of the cavity. The potential outside the cavity is expanded in irregular spherical harmonics I_L defined as

$$I_L(\mathbf{r}_J) = r_J^{-(l+1)} C_l^m(\theta_J,\varphi_J) \tag{6}$$

where r_J, θ_J and φ_J are the polar coordinates of the vector $\mathbf{r}_J$ which has its origin at center J and which defines a point P. $C_l^m(\theta_J,\varphi_J)$ denotes the Racah spherical harmonics [10, 12] . This expansion with unknown coefficients γ_L takes the form:

$$V_o(P) = \sum\nolimits_J\sum\nolimits_L \gamma_L(J) I_L(\mathbf{r}_J) \tag{7}$$

The potential inside the cavity is the sum of the potential created by the multipoles and the reaction potential due to the polarization of the solvent. The latter is expressed on a basis of solid spherical harmonics

$$S_L(\mathbf{r}_J) = r_J^l C_l^m(\theta_J,\varphi_J) \tag{8}$$

The whole potential inside the cavity can be written:

$$\begin{aligned}V_i(P) = \sum\nolimits_J\sum\nolimits_L \Big[& M_L(J) I_L(\mathbf{r}_J) \\ & + \sum\nolimits_K R_L(K,J) S_L(\mathbf{r}_J)\Big]\end{aligned} \tag{9}$$

For a point σ on the surface of the cavity and if ε is the dielectric constant of the continuum, the electrostatic conditions are written:

$$V_i(\sigma) = V_o(\sigma) \tag{10a}$$

$$[\nabla V_i(\sigma)]_n = \varepsilon\,[\nabla V_o(\sigma)]_n \tag{10b}$$

where the subscript n indicates the component of the field normal to the surface and ε is the dielectric constant of the solvent.

The second derivatives of Eqs. (10a) and (10b) with the definitions (7) and (9) leads us to two linear equations in which the only unknowns are the second derivatives of γ_L and of $R_L(K,J)$. The procedure adopted to compute these derivatives is analogous to that developed for the computation of the reaction field factors and the first derivatives of energy [11]. The computation consists in defining an overdetermined set of linear equations by considering as many points on the surface of the cavity, usually 1,500 or more, to compute the derivatives with a great accuracy.

Implementation

The whole computational procedure has been implemented in our home copy of the Gaussian03 suite of programs [16] and can work at the Hartree–Fock, post Hartree–Fock and DFT levels of computation. The cavity is defined by the solvent accessible surface build with the help of the GEPOL program [14,15] in which the Bondi atomic radii are multiplied by a factor $\alpha = 1.308$.

Test of the method

In order to verify the reliability of the method and the performances of the code, a first test has been performed on a reference molecule: formaldehyde, on which detailed experimental data are available. The shift of the CO stretching frequency ν(CO) is computed, in the harmonic approximation, with several methods: our previous single center multipole expansion (SC), both distributed multiplole expansions: GAD and MSP and finally with the PCM model, as implemented in Gaussian 98, with the default option and with the same definition of the cavity as in the present model. Similarly we tested the PCM model as implemented in Gaussian 03, with the default options: Integral Equation Formalism (IEF) and the volume of the cavity is defined by the Simple United Atom Topological Model (UAO), compared with the same option with the Bondi radii augmented as above.

Table 1 Solvent effect on the ν(CO) frequency of formaldehyde

Solvent	Model	Volume (Å^3)	E_{solv} (kcal/mol)	$\nu(\mathrm{CO})_{\mathrm{calc}}$ (cm^{-1})	$\nu(\mathrm{CO})_{\mathrm{exp}}$ (cm^{-1})	$\Delta\nu^{\mathrm{a}}_{\mathrm{calc}}$ (cm^{-1})	$\Delta\nu^{\mathrm{b}}_{\mathrm{exp}}$ (cm^{-1})
Vacuum			0.0	1,827.1	1,746	0.0	
	SC	58.72	−1.12	1,817.0		−10.1	
	GAD	59.10	−1.13	1,816.2		−10.9	
	MSP	59.65	−1.14	1,816.2		−10.9	
Cyclohexane	PCM 98[c]	102.84	−0.71	1,824.8	1,735	−2.3	−11
	PCM 98[d]	60.37	−1.15	1,819.0		−8.1	
	PCM 03[e]	56.73	−1.42	1,810.2		−16.9	
	PCM 03[f]	45.75	−1.73	1,808.1		−19.0	
	SC	59.76	−3.10	1,802.3		−24.8	
	GAD	59.76	−3.10	1,801.4		−25.7	
	MSP	59.74	−3.11	1,800.9		−26.2	
Acetonitrile	PCM 98(c)	102.86	−1.89	1817.5	1,723	−9.6	−23
	PCM 98(d)	60.37	−3.17	1,808.3		−18.8	
	PCM 03(e)	56.74	−4.15	1,783.0		−44.1	
	PCM 03(f)	45.77	−5.05	1,777.5		−49.6	

SC single center expansion; *GAD* Gaussian averaged distribution; *MSP* Mulliken Sokalski Poirier distribution (see text)

[a] $\Delta\nu = [\nu(\mathrm{CO})_{\mathrm{solv}} - \nu(\mathrm{CO})_{\mathrm{vacuum}}]$

[b] Reference [17]

[c] Gaussian-98 PCM, default ($\alpha = 1.4$)

[d] Gaussian-98 Option: IEF, radius Bondi, $\alpha = 1.308$

[e] Gaussian-03 PCM default (IEF, radius UAO, $\alpha = 1$)

[f] Gaussian-03 Option: IEF, radius Bondi, $\alpha = 1.308$

Table 2 Solvent effect on the ν(CO) frequency of benzophenone

Solvent	E_{solv} (kcal/mol)	ν(CO) (cm^{-1})	ν(CO), [a] scaled (cm^{-1})	$\nu(\mathrm{CO})_{\mathrm{exp}}$ (cm^{-1})
Vacuum	0.	1,750.5	1,706.2	
n hexane $\varepsilon = 1.92$	−1.36	1,741.0	1,696.9	1,696.4[b]
$CCl_4\varepsilon = 2.228$	−1.71	1,738.7	1,694.7	1, 691.0[c]
Chlorobenzene $\varepsilon = 5.621$	−3.17	1,730.3	1,686.5	1,687.5[b]
THF $\varepsilon = 7.58$	−3.49	1,729.0	1,685.3	1,689.2[b]
DMSO $\varepsilon = 46.7$	−4.36	1,725.0	1,681.4	1,682.0[c]

[a] Scaling factor: 0.9747

[b] Reference [19]

[c] Reference [20]

The unscaled results are listed in Table 1. They show a good agreement between the experimental and the computed frequency shifts in the case of the SD, GAD and MSP multipole expansions, in particular if one remembers that the harmonic approximation, in the DFT formalism, usually leads to an overestimation of the frequencies. The various versions of the PCM model give different results. If one refers to the Onsager prescription [18], the volume of the cavity should be close to the molecular volume in the liquid state. In the case of formaldehyde this volume, estimated at −20°C, should be of the order of 60 Å^3 . The cavity volumes obtained with our models and by the default PCM model implemented in Gaussian 03 are close to this value. This is also true for the PCM model implemented in Gaussian 98 when the scaled Bondi radii are used contrarily to the default option which uses a larger cavity. Regarding the frequency shifts introduced by the solvent, the computations performed with Gaussian 03 overestimate the solvent effect. This is probably partly due to the size of the cavity which is too small, but there may be an additional cause of discrepancy since the default option, which overestimates substantially the solvent effect, uses a reasonable cavity. These observations, which have been done on other molecules, liquid at room temperature in order to have a better reference for the volume of the cavity, seem to be general. From this comparison, one deduces that care should be taken when using the PCM model as implemented in the Gaussian codes, at least regarding the solvent effects in vibrational spectroscopy.

Another test has been conducted on a larger molecule for which some experimental data are available: acetophenone. The CO stretching frequency ν(CO) has been computed in a series of solvents, with the help of GAD, and the computed frequencies compared with the experimental ones after rescaling. The results, for five solvents of increasing dielectric constant: *n* hexane, carbon tetrachloride (CCl_4), chlorobenzene, tetrahydrofurane (THF) and dimethylsulfoxide (DMSO) are listed in Table 2. They show that a scaling factor of 0.9747 makes the computed frequencies very close to the experimental one. The worse agreement is observed in the case of the THF solution, but one notices that the exper-

Table 3 Solvent effect on the ν(CN) frequency of benzonitrile ($X = \mathrm{H}$)

Solvent	E_{solv} (kcal/mol)	$d(\varphi$–C) (Å)	d(CN) (Å)	ν(CN) (cm^{-1})	ν(CN) scaled[a] (cm^{-1})	$\nu(\mathrm{CN})_{\mathrm{exp}}$ (cm^{-1})[b]
Vacuum	0.	1.431	1.155	2,339.0	2,236.4	
n hexane	−1.87	1.431	1.155	2,335.6	2,233.1	2,233.20
CCl_4	−2.30	1.431	1.155	2,335.0	2,232.5	2,231.50
THF	−4.44	1.430	1.156	2,332.1	2,229.7	2,230.15
DMSO	−5.42	1.430	1.156	2,330.9	2,228.5	2,228.67

[a] Scaling factor 0.9561

[b] Reference [21]

Table 4 Solvent effect on the ν(CN) frequency of para chloro benzonitrile ($X =$ Cl)

Solvent	E_{solv} (kcal/mol)	$d(\varphi$–C) (Å)	d(CN) (Å)	$d(\varphi$–X) (Å)	ν(CN) (cm^{-1})
Vacuum	0.	1.430	1.155	1.753	2,340.4
n Hexane	−1.80	1.430	1.155	1.755	2,337.4
CCl_4	−2.28	1.430	1.155	1.755	2,337.0
THF	−4.26	1.430	1.155	1.756	2,334.8
DMSO	−5.18	1.430	1.155	1.756	2,334.0

Table 5 Solvent effect on the ν(CN) frequency of para amino benzonitrile ($X = NH_2$)

Solvent	E_{solv} (kcal/mol)	$d(\varphi$–C) (Å)	d(CN) (Å)	$d(\varphi$–X) (Å)	ν(CN) (cm^{-1})
Vacuum	0.	1.427	1.156	1.381	2,328.6
n Hexane	−3.17	1.426	1.157	1.376	2,321.8
CCl_4	−3.96	1.425	1.157	1.375	2,320.3
THF	−7.87	1.424	1.158	1.372	2,313.0
DMSO	−9.71	1.423	1.158	1.371	2,309.6

imental frequency is larger than the observed value in the case of the solution in chlorobenzene, in contradiction with what is expected for a purely electrostatic phenomenon. The same observation is done for the ν(CO) frequency of benzophenone in the same solvents [19]. This could indicate some specific solute-solvent interactions which are not taken into account by the electrostatic models.

With regard to the efficiency of the codes, the time, on a IBM pSeries 630 workstation, for the geometry optimization starting from the gas phase structure is of 59 min 31 s, 55 min 44 s and 56 min 50 s with the GAD, MSP and PCM (with Gaussian 03) models respectively, and the computation of the vibrational frequencies takes, respectively, 1 h 24 min 03 s, 1 h 15 min 30 s and 1 h 22 min 06 s. It is therefore difficult to say that, for the computational time, one model is better than the others. Gaussian 98 requires much greater computer time.

Application: solvent effect on the CN stretching frequency of para-substituted benzonitriles

The role of various π electron donating subtituents: Cl, NH_2, $N(CH_3)_2$ and one-electron acceptor group: NO_2 at the para position of benzonitrile (Schemes 1 and 2) on the CN stretching frequency ν(CN) has been chosen to illustrate the chemical information which may arise from a detailed analysis of solvent effects. Table 3 gives the results obtained with the GAD model on the unsubstituted molecule, for which some experimental data are available [21]. Tables 4, 5, 6 and 7 are relative to the substituted molecules. These tables give the stretching frequency, the solvation energy and some geometric data which characterize the modifications of the electronic structure of these molecules under the influence of the solvent. These data are the distance $d(\varphi$–C) between the carbon atom of the CN group and the carbon atom of the ring bonded to it, the bond length d(CN) of the nitrile group and the distance $d(\varphi$–$X)$ between the para atom of carbon of the ring and the atom of the substituent X bonded to it.

In the case of benzonitrile one notices that by using a single scaling factor of 0.9561 the agreement between the computed frequencies and the available experimental ones is pretty good. For this solute and the molecules substituted with an electron donating group, one notices that the frequency ν(CN) diminishes with increasing polarity of the solvent, and this effect is accompanied, as expected [3], by an increase on the CN bond length. In the meantime the distance d(φ–C) diminishes in all the molecules of the family, even in the case X = Cl where the effect would be visible on the fourth decimal which has been removed from the tables. This behavior is characteristic of an increase of the electron transfer to the nitrile group under the influence of the reaction field. The transfer from the substituent induces a shortening of the φ–X bond length, which is very visible in the case of the amino and dimethylamino derivatives. In the case of the chloro derivative, this bond length behaves differently, but

Table 6 Solvent effect on the ν(CN) frequency of para dimethylamino benzonitrile ($X = N(CH_3)_2$)

Solvent	E_{solv} (kcal/mol)	$d(\varphi\text{–C})$ (Å)	d(CN) (Å)	$d(\varphi\text{–}X)$ (Å)	ν(CN) (cm^{-1})
Vacuum	0.	1.426	1.157	1.375	2,325.7
n Hexane	−2.74	1.424	1.158	1.371	2,313.4
CCl_4	−3.40	1.424	1.158	1.370	2,312.4
THF	−6.71	1.422	1.158	1.367	2,307.8
DMSO	−8.28	1.422	1.158	1.365	2,305.6

Table 7 Solvent effect on the ν(CN) frequency of para nitro benzonitrile ($X = NO_2$)

Solvent	E_{solv} (kcal/mol)	$d(\varphi\text{–C})$ (Å)	d(CN) (Å)	$d(\varphi\text{–}X)$ (Å)	ν(CN) (cm^{-1})
Vacuum	0	1.431	1.155	1.484	2,343.7
n Hexane	−2.36	1.432	1.155	1.482	2,339.6
CCl_4	−2.92	1.432	1.155	1.482	2,339.7
THF	−5.62	1.431	1.155	1.480	2,340.5
DMSO	−6.85	1.431	1.155	1.480	2,340.7

Table 8 Solvent effect on the electronic properties of para nitro benzonitrile ($X = NO_2$)

Solvent	$\mu(D)$	Charge O (NO_2)	Charge NO_2	Charge CN	Charge N (CN)
Vacuum	0.0716	−0.257	−0.339	−0.154	−0.201
n hexane	0.0362	−0.266	−0.357	−0.197	−0.229
CCl_4	0.0345	−0.267	−0.375	−0.199	−0.233
THF	0.0150	−0.276	−0.373	−0.182	−0.251
DMSO	0.0075	−0.279	−0.376	−0.161	−0.256

one also notices that the solvation energy increases less than in the case of the unsubstituted nitrile. This may be explained by the strong σ polarization of the C–Cl bond which creates a local dipole moment opposite to the molecular moment and a local reaction field, rather strong because the chlorine atom is close to the solvent, which increases this polarization. In fact the total Mulliken charge of the chlorine atom varies from −0.04 in a vacuum to −0.06 in DMSO.

The case of para nitro benzonitrile appears very interesting. One notices on Table 7 that the CN stretching frequency does decrease when passing from the gas phase to the solution in cyclohexane but then, in contradiction with the other solutes, it increases slightly when the dielectric constant of the solvent increases. If one looks at the dipole moment of the solute (Table 8), it decreases with the increasing polarity of the solvent and even exhibits a change of sign in water, contrarily to the usual behavior which is generally characterized by an increase of the dipole moment of the solute due to the polarizing effect of the reaction field. The explanation can be found by considering the opposite effects of the two-electron acceptor groups and the local perturbation due to the reaction field. This field acts more strongly on the nitro group than on the nitrile group, thanks to the important negative charge on the oxygen atoms, and the consequence is that this negative charge becomes larger and larger when the dielectric constant of the solvent increases as one can see on Table 8. The result is that the nitro group becomes more and more electron attracting when the polarity of the solvent increases. The negative charge of the nitrile group first increases in non polar solvents but decreases when the dielectric constant increases, although the negative charge of the nitrogen atom still increases. The consequence of this loss of electrons by the nitrile group is a slight shortening of the CN bond contrarily to what one observes in the case of the other nitriles.

Conclusion

The use of distributed multipoles in the formalism of the reaction field factors allowed us to develop an efficient code which permits quantum chemical computations on solutes solvated by a continuum. The computation of the second energy derivatives makes possible the computation of vibrational frequencies in the harmonic approximation and, on the test systems, one could verify that the solvent effects on some infrared bands agrees well with the experimental data owing to the approximations done.

An original study of the solvent effects on some para substituted benzonitriles shows that an analysis of the role of the solvent, made possible by the use of such a code, provides us with a detailed picture of the electronic effects occurring in solution and allows us to better understand the modifications of the vibrational spectra.

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References

1. Pulay P (1995) Adv Ser Phys Chem 2:1191
2. Rauhut G, Pulay P (1995) J Phys Chem 99:3093
3. Rivail JL, Rinaldi D, Dillet V (1998) Mol Phys 89:1521
4. Dillet V, Rinaldi D, Bertrán J, Rivail JL (1996) J Chem Phys 104:9437
5. Miertus S, Scrocco E, Tomasi J (1981) Chem Phys 55:117
6. Miertus S, Tomasi J (1982) Chem Phys 65:239
7. Klamt A, Schüürmann GJ (1993) J Chem Soc Perkins Trans 2(2):799
8. Stone AJ (1985) Chem Phys Let 83:233
9. Stone AJ (1985) Mol Phys 56:1065
10. Stone AJ (2000) The theory of intermolecular forces. Oxford University Press, Oxford
11. Rinaldi D, Bouchy A, Rivail JL, Dillet V (2004) J Chem Phys 120:2343
12. Gray CG (1976) Can J Phys 54:505
13. Stone A, Tough RJA (1984) Chem Phys Let 110:123
14. Pascual-Ahuir JL, Silla E (1990) J Comp Chem 11:1047
15. Silla E, Tuñón I, Pascual-Ahuir JL (1991) J Comp Chem 12:1077
16. Gaussian 03, Revision B.05, Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery JA Jr, Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA (2004) Gaussian, Inc., Wallingford CT
17. Wong MW, Wiberg KB, Frisch MJ (1991) J Chem Phys 95:8991
18. Onsager L (1936) J Am Chem Soc 58:1486
19. Garcia MV, Redondo MI (1987) Spectrochim Acta 43A:879
20. Nyquist RA, Chrzan V, Houck J (1989) Appl Spectrosc 43:981
21. Kolling OW (2000) Appl Spectrosc 54:890