



Force Constant Optimization of *trans* Nitrous Acid Based on Classical Wilson Method Using Root Mean Square as Measuring Criteria

MUSA E. MOHAMED BABIKER^{1,2,*}

¹Department of Chemistry, Faculty of Science, Al-Baha University, P.O. Box: 1998, Al-Baha, Kingdom of Saudi Arabia

²Department of Chemistry, College of Applied and Industrial Sciences, University of Bahri, Khartoum, Sudan

*Corresponding author: Tel: +966 558841537; E-mail: musa.elballa@gmail.com

Received: 29 February 2016;

Accepted: 3 June 2016;

Published online: 30 June 2016;

AJC-17974

Optimization method for the force constants based on the classical Wilson method but use the gold method for bracketing the force constant as a function of the fitness of the calculated and experimental spectra determined by the root mean square criteria. The optimization of force constants of *trans* nitrous acid has been carried out using the Wilson's methods of F and G matrices and quantum mechanics. The minimum root mean square (rms) by GF matrix methods was found to be 0.5121 cm⁻¹ for HONO, 1.4283 cm⁻¹ for HON¹⁵O, 3.6561 cm⁻¹ for HO¹⁸NO¹⁸, 14.4696 cm⁻¹ for DONO and 13.4152 cm⁻¹ for DON¹⁵O. The (root mean square) by quantum mechanics was found to be 180.3, 53.09, 29.20 and 27.16 cm⁻¹ for *trans* nitrous acid by PM3, MP2/6-31G(d), B3LYP/6-31+G(d) and B3LY/6-31G(d), respectively.

Keywords: Force constant, *Trans* nitrous acid, Root mean square, GF matrix method.

INTRODUCTION

Wilson's GF method, sometimes referred to as GF method, is classical method to obtain internal coordinates for a vibrating semi-rigid molecule; the so-called normal coordinates [1]. Normal coordinates decouple the classical vibration motions of the molecule and thus give an easy route to obtain vibration amplitudes of the atom as function of time. In Wilson's GF method it is assume that the molecular kinetic energy consists only of harmonic vibrations atoms, *i.e.* overall rotational and translational energy is ignored [1].

It is possible to write the quantum mechanical kinetic energy operator for the curvilinear coordinates, but it is hard to formulate a general theory applicable to any molecule. This is the reason so that Wilson [2] made the internal coordinates linear by assuming small displacements. There is a quantitative problem of how the frequencies of the molecular vibrations, which can be obtained by experiment, are related to the masses of the atoms, the bond angles and bond lengths and most particularly the force constants of the individual bonds and inter bond angles. In this work we shall adopt, Wilson's methods of F and G matrices [1,3], which is generally the method adopted in chemical problems. All of the required relations are combined in matrix equation and solved as an Eigen value problem:

$$|FG - E\lambda| = 0$$

In which F, G and E are matrices and the entire left-hand side of the equation is a determinant. F is a matrix of force constants and thus brings the potential energies of the vibration into the equation as a matrix, the G matrix involves the masses and certain spatial relationships of the atoms and thus brings the kinetic energy into the equation. E is the unit matrix and λ , the Eigen value of matrix product FG, brings the frequency, ν , into the equation, is defined by:

$$\lambda = 4\pi^2c^2\nu^2$$

The values of the elements of the G matrix of any molecule have been calculated using the masses and certain relationships of the atoms [3]. From the relation $\lambda = 4\pi^2c^2\nu^2$ the frequency is calculated. In summary we have the experimental geometry to set up the G matrix and the experimental frequencies corresponding to the Eigen values. We need a good guess for the force constants and optimize it until the experimental and calculated frequencies coincide so as to obtain the best force constants.

The refinement of the intermolecular force field is a difficult test for larger molecules. There are too many parameters to be determined and too many choices among the sets of parameters values that can reproduce the experimental vibration levels. The choices are significantly reduced by the use of the isotope data effects on the energy levels and the vibration-rotation interaction constants. However, they are forced to be

further reduced on a more priority basis, *i.e.*, by assuming transferability of force constants among similar molecules and/or by imposing on the force field a certain physical model, which is more or less arbitrary. The final force fields resulting from these calculations are often found to depend on the initial force fields. The diagonal force constants may reasonably be transferred among structurally related molecules but such a transfer is difficult in the case of off-diagonal force constants, since they depend greatly on the nature of the molecules. The interaction force constants also play an important role in determining the total force field as well as the potential energy distributions (PED) of a molecule. Hence, it is essential to consider reliable values for these force constants while constructing the initial force field.

Determination of a suitable set of force constants for a molecule from its observed vibration frequencies in starts with a good guess borrowed from similar molecules, assuming reproducibility of the force field, F° . With a good experimental molecular geometry the Eigen values of GF° correspond to the calculated frequency parameters as follows:

$$\lambda(\text{cal}) = 4\pi^2 [\nu(\text{cal})]^2$$

In most cases the frequency calculated do not agree with the observed frequencies and force constant must be refined by iteration until the quantities $\Delta\lambda = \lambda(\text{cal}) - \lambda(\text{obs})$ vanish. If F° is well chosen, the $\Delta\lambda$'s will be small and the first-order perturbation theory will provide the needed correction to the F matrix [4]. Thus,

$$G(F^\circ + \Delta F)L^\circ \approx L^\circ \Lambda_{\text{obs}} \quad (1)$$

$$G(\Delta F)L^\circ \approx L^\circ (\Delta\lambda_{\text{cal}} - \Lambda_{\text{obs}}) = L^\circ (\Delta\Lambda) \quad (2)$$

Since $L^\circ L^{\circ\top} = G$ eqn. (2) can be written in the form:

$$L^\circ(\Delta F)L^\circ \approx \Delta\Lambda \quad (3)$$

In this equation, it is immediately seen that the coefficients of the elements of ΔF are simply the elements of the Jacobian of Λ with respect to F. Hence, eqn. 3 can be rewritten as:

$$J(\Delta F) \approx \Delta\Lambda \quad (4)$$

Eqn. 4 forms the basis of the iteration method [4].

The only efficient way to calculate force constants from frequencies is to use an iterative computational approach. To do this a starting set of assumed force constants is refined by successive approximations until the set which yields calculated frequencies is in best agreement with observed ones is obtained.

Force constant optimization by quantum mechanics:

In recent years, quantum mechanical methods have proven to be quite useful in evaluating vibration force fields [5]. It is often observed that vibration frequencies computed using quantum mechanical methods are higher in energy than experimental values. The discrepancy between the computed and experimental force constants is sufficiently systematic to permit the application of generalized scaling procedures, which bring the computed spectrum into agreement with experiment [6]. The determination of appropriate scale factors work is well except in cases where the vibrations are sensitive to the off-diagonal elements or when correlation effects are large [7,8]. For such systems, refinement of structural models is achieved by evaluating force fields at increasingly higher levels of theory

[9]. For a molecule that is too large to be handled by *ab initio* methods or when rapid and inexpensive solutions are required, semi empirical methods offer a compromise between cost and computational accuracy [10]. The most comprehensive study of semiempirical calculations using AM1 method by Healy and Holder [11] on 42 common organic molecules in which the computed harmonic frequencies were found to differ from experimental by an average of 10.4 %.

Pople *et al.* [12] found that the harmonic vibration frequencies calculated at HF/3-21G for a set of 38 molecules (477 frequencies), which suggested that this level of theory overestimates frequencies by about 12 %. A scaling factor of 0.89 for theoretical HF/3-21G harmonic frequencies are proposed as being appropriate for predictive purposes. Hehre *et al.* [13] determine from HF/6-31G(d) study of 36 molecules a mean percentage deviation of theoretical harmonic frequencies from experimental fundamental of about 13 % similar to the findings of Pople *et al.* [12] for HF/3-21G. An HF/6-31G (d) theoretical frequency scaling factor of 0.8929 has been widely used [14]. Some workers [6] found that the overall root-mean-square (rms) errors for the MP2-fu/6-31G(d) was only slightly smaller than the overall rms error for the HF/6-31G(d) level of theory. The advent of density functional theory (DFT) has provided a correlation in the study of the vibration frequencies of moderately large molecules [15]. Pople *et al.* [16] have shown that B-LYP/6-31G(d) harmonic vibration frequencies reproduce observed fundamentals with surprising accuracy. They found, for example an average error of only 13 cm^{-1} for a small set of molecules with up to three heavy atoms. Rauhut and Pulay [17] developed scaling factors for the B-LYP/6-31G(d) methods based on a set of 20 small molecules with a wide range of functional groups. Their overall frequencies scaling factor for the B-LYP/6-31G(d) method was determined to be 0.990 with an rms deviation of 26 cm^{-1} . Slightly lower rms deviation of 19 cm^{-1} was determined by Finley and Stephens [18].

Nitrous acid: Nitrous acid (HONO) plays an important role in atmospheric chemistry. It is one of the smallest molecules which exhibits a *cis-trans* conformational equilibrium and has been studied extensively to obtain molecular geometries and force fields by infrared and microwave spectroscopic methods [19]. For these reasons it has been of significant interest both theoretically [20] and experimentally [19]. Microwave studies have shown that the *trans* form of the molecule is more stable than the *cis* form by 1.6 KJ/mol with an estimated barrier of inter conversion of approximately 40 kJ/mol [21]. These results are fairly consistent with earlier experimental results and with *ab initio* calculations [20].

Force constants calculation of *trans* nitrous acid were reported by Palm [22], were fitted by a least-squares method, in which the diagonal valence force constants were taken as the starting set and a minimum number of off diagonal interaction constants were introduced to the best fit of frequencies. The final sets of force constants obtained from these calculations with rms = 6.59 cm^{-1} are listed in Table-1 [23]. *ab initio* calculated harmonic frequencies for *trans* nitrous acid [24,25], using the quadratic configuration including singles and doubles with polarized split-valence basis sets QCISD/6-311+G* level of

TABLE-1

FORCE CONSTANT FOR *trans* NITROUS ACID, STRETCH CONSTANTS IN MILLIDYNES PER ANGSTROM, BEND CONSTANTS IN MILLIDYNES*ANGSTROM PER SQUARE RADIAN AND STRETCH-BEND INTERACTION CONSTANTS IN MILLIDYNES PER RADIAN, AT rms = 6.5955 cm⁻¹ [Ref. 23]

Force constant	Value
f (N=O)	12.0400
f (N-O)	3.0840
f (H-O)	7.2450
f (ONO)	1.5880
f (HON)	0.7647
f (HONO)	0.1295
f (NO)(ONO)	0.4023

theory, with a greater value of rms between experimental and calculated frequencies, rms is 125.35, 99.227 cm⁻¹ for HONO [24,25] and 85.05 cm⁻¹ for DONO [24]. The infrared spectra of isotopic *trans*-nitrous acid molecules including ¹⁵N, D and ¹⁸O species have been obtained in the vapour and in the solid phases. The vibrational frequencies of isotopic *trans* nitrous acid have been calculated [23] with empirical force field method, rms as follows; 9.7553 cm⁻¹ for DONO, 7.1995 cm⁻¹ for HON¹⁵O, 8.7369 cm⁻¹ for DON¹⁵O, 9.1924 cm⁻¹ for HO¹⁸NO¹⁸.

EXPERIMENTAL

GF method: The initial values of F matrix elements were obtained from the literature work [26]. Geometrical parameters for *trans* nitrous acid was obtained from microwave spectra [27]. MATLAB 7.0 [28] program was used to solve the secular equation:

$$|FG - AE| = 0$$

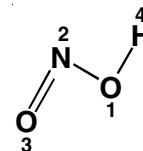
The initial values were refined manually by adding $\pm 0.1-0.003$, to the diagonal values of the initial values of force constant starting from the f_{11} , until the minimum value of root mean square (rms) between observed and calculated frequencies was obtained and the methods was then repeated until consistency.

Quantum mechanical method: Geometry optimization, vibration frequencies and harmonic force constants fields of *trans*-nitrous acid were calculated by Semi empirical and *ab initio* method, the semi empirical method PM3 was performed with MOPAC2007 [29] on a personal computer. The PM2 and DFT calculations were carried out using the Gaussian 09 [30] program package. The basis sets 6-31G(d) and 6-31+G(d), were used with B3LYP and PM2 for comparison purposes. The B3-LYP exchange-correlation density functional was employed in the present study, which contains gradient corrections for both exchange and correlation. The optimized geometries were used as the reference geometries for calculations of force constants and vibration frequencies.

RESULTS AND DISCUSSION

The general molecular structure of *trans* nitrous acid is shown in Fig. 1. The values of the initial force constant for *trans* nitrous acid used are as follows (in mydn/Å⁻¹), $f_{11}(\text{OH}) = 7.18$, $f_{22}(\text{N=O}) = 12.28$, $f_{33}(\text{N-O}) = 2.22$, $f_{44}(\text{NOH}) = 0.76$, $f_{55}(\text{ONO}) = 2.45$, $f_{23} = 1.67$, $f_{24} = 0.12$, $f_{34} = 0.04$, $f_{35} = 0.41$, f_{45}

$= 0.14$, $f_{66}(\text{torsion}) = 0.131$. The equilibrium microwave geometry [25] of *trans* nitrous acid used in this work is as follows (Å), O-H = 0.954, N-O = 1.433, N=O = 1.163, ONO angle = 110.7°, NOH angle = 102.1°, dihedral angle = 180° [25]. The rms of the initial force constant was calculated (as 22.656 cm⁻¹).

Fig. 1. Molecular structure of *trans*-nitrous acid

The values of optimized force constant and calculated frequencies for *trans* nitrous acid have been shown in Tables 2 and 3, respectively. The frequencies for isotopic nitrous acid were also calculated by the above method, with isotopic mass, D = 2.0141022, ¹⁵N = 15.000108, ¹⁸O = 17.9991598. Four isotopes of *trans* nitrous acid were selected for optimization; DONO, HON¹⁵O, DON¹⁵O and HO¹⁸NO¹⁸ with observed vibration frequencies [23], the rms were, 14.4696 cm⁻¹ for DONO, 1.4283 cm⁻¹ for HON¹⁵O, 13.4152 cm⁻¹ for DON¹⁵O, 3.6561 cm⁻¹ for HO¹⁸NO shown in Table-4.

TABLE-2
CALCULATED FORCE CONSTANT BY GF MATRIX
FOR *trans*-NITROUS ACID AT rms = 0.5121

Initial diagonal force constant	Diagonal optimized force constant	Cross terms optimized force constant
F ₁₁ 7.18	F ₁₁ 7.242	F ₂₃ 1.670
F ₂₂ 2.22	F ₂₂ 2.226	F ₂₄ 0.040
F ₃₃ 12.28	F ₃₃ 12.343	F ₂₅ 0.410
F ₄₄ 0.76	F ₄₄ 0.770	F ₃₄ 0.120
F ₅₅ 2.45	F ₅₅ 2.467	F ₄₅ 0.140
F ₆₆ 0.131	F ₆₆ 0.132	-

TABLE-3
CALCULATED VIBRATION FREQUENCIES BY GF
MATRIX FOR *trans* NITROUS ACID AT rms = 0.512

Observed vibration frequencies	Calculated vibration frequencies	Vibration mode
v ₁ 3588	3588.1	v(O-H)
v ₂ 1699	1699.1	v(N=O)
v ₃ 1265	1263.8	v(HON)
v ₄ 791	790.7	v(NO/ON)
v ₅ 593	593.1	v(ONO/NO)
v ₆ 540	540.2	Torsion

The observed and calculated vibration frequencies of *trans* nitrous acid by GF matrix methods are given in Table-3. The results show that there is almost congruence between calculated and observed vibration frequencies when our method of optimization of force constant is used. The root mean square was found to be 0.5121 cm⁻¹ for HONO, less than that calculated by empirical force field method (rms = 6.5955 cm⁻¹ [23]), by quantum mechanics (rms = 99.227 cm⁻¹ [27], 125.3598 cm⁻¹ [24]).

Comparison of the results of the isotopes of the *trans* nitrous acid (Table-4), with empirical force field method as rms is 1.4283 cm⁻¹ for HON¹⁵O (7.1995 cm⁻¹ [23]), 3.6561

TABLE-4
CALCULATED VIBRATION FREQUENCIES BY GF MATRIX FOR ISOTOPES OF *trans* NITROUS ACID

Mode	DONO		HON ¹⁵ O		DON ¹⁵ O		HO ¹⁸ NO ¹⁸	
	Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated
ν_1	2648	2615.5	3588	3588.1	2646	2615.4	3571	3575.9
ν_2	1692	1691.9	1669	1667.3	1661	1659.9	1666	1659.5
ν_3	1014	1003	1261	1262.7	1008	997.8	1251	1250.7
ν_4	737	733.4	774	776.3	723	723.5	779	775.7
ν_5	586	586.7	589	589.2	583	582.4	564	565.5
ν_6	416	408	538	539.2	413	406.7	537	537.7

cm^{-1} for HO¹⁸NO¹⁸ (9.1924 cm^{-1} [23]), 14.4696 cm^{-1} for DONO (9.7553 cm^{-1} [23], 85.05 cm^{-1} [24]) and 13.4152 cm^{-1} for DON¹⁵O (8.7369 cm^{-1} [23]). The rms is generally lower by our method except for DONO isotope due to the high primary deuterium isotope effect.

The diagonal set of optimized force constants for *trans* nitrous acid in internal coordinate are given in Table-2. RMS at initial set of diagonal force constants for *trans* nitrous acid was 22.6557 cm^{-1} , improvements to rms 6.100 cm^{-1} was obtained by diagonal force constants, while further improvements to 0.5121 cm^{-1} was obtained after the introduction of the off diagonal force constants. The latter are responsible for the interaction between internal coordinates among themselves like bond-bond, bond-angle and bond-dihedral interactions.

The use of the root mean square as optimization function is new and only used in this work. The idea depends on the fact that having used a good guess initial force constant the rms oscillates along a parabola from an equilibrium value (Fig. 2). This applies to all the force constants and can be transferred from one force constant to another. The first cycle of optimization reduces the rms quite considerably. Further cycles refine the value and as is case in all iterative procedures a tolerance value is used as a seeking. Force constants are acceptably refined to within 10^{-4} millidyne per angstrom.

The background of the optimization involving the parabolic oscillation of rms is based on the bracketing of the independent variable (the abscissa) which is here the force constant and minimize the dependant function (the rms). As long as we are using the rms to fit a calculated frequency to the observed frequency then the function is bound and the force constant is without rigorous proof automatically bound

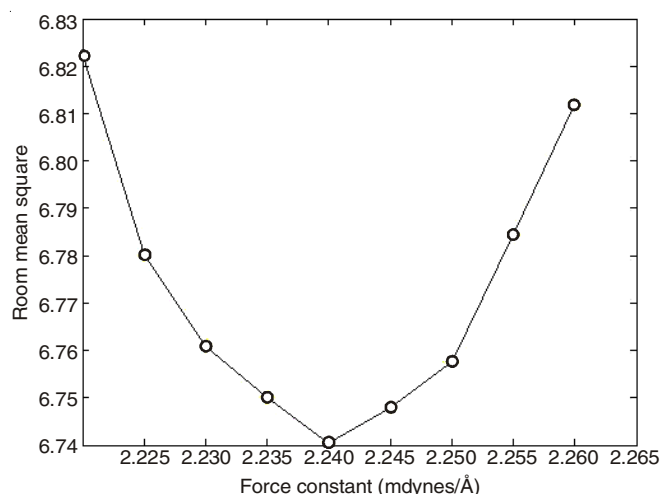


Fig. 2. Root mean square rms in cm^{-1} vs. force constant $f(\text{N-O})$ of *trans* nitrous acid

which makes the bracketing accessible with an interval (a,b). In this work we applied the minimization manually. Many algorithms are available for function optimization *e.g.* golden section search and simplex method.

Table-5 compares the theoretical geometry of *trans* nitrous acid with experimental values. The semi empirical geometry is poor as expected. The best method in semiempirical is PM3 as compared to AM1. The agreement is significantly better at the *ab initio* methods. The introduction of density functional B3LYP and Møller-Plesset Methods improve the geometry. The optimized geometries were used to calculate the vibration frequencies and force constant, which were scaled to give good agreements with observed frequency, using scale factors of

TABLE-5
OPTIMIZED GEOMETRIES OF *trans* NITROUS ACID (Å AND °) CALCULATED AT DIFFERENT LEVEL OF THEORY COMPARED WITH EXPERIMENTAL ONE

Method	HO	ON	N=O	HON	ONO	Torsion	ΔH
PM3	0.950	1.383	1.167	104.56	138.64	180.00	-14.91
MP2/6-31G(d)	0.979	1.425	1.197	101.85	110.31	180.00	-205.17
B3LYP/6-31+G(d)	0.977	1.426	1.177	103.00	110.89	179.99	-205.71
Experimental	0.954	1.433	1.163	102.10	110.7	180.00	-

TABLE-6
SCALED^a CALCULATED VIBRATION FREQUENCIES (cm^{-1}) OF *trans* NITROUS ACID COMPARED WITH EXPERIMENTAL VALUES

Method	Torsion	$\nu(\text{ONO/NO})$	$\nu(\text{NO/ON})$	$\nu(\text{HON})$	$\nu(\text{N=O})$	$\nu(\text{OH})$	rms
PM3	417	593	863	1396	2008	3838	180.3
MP2/6-31G(d)	579	597	829	1258	1591	3541	53.09
B3LYP/6-31+G(d)	565	600	796	1257	1707	3528	27.16
Experimental	540	593	791	1265	1699	3588	-

^aThe scale factor for PM3 = 0.9761 [Ref. 6], for *ab initio* methods is 0.957.

TABLE-7
 SCALED^a CALCULATED FORCE CONSTANTS IN INTERNAL COORDINATES (mdynes/Å) OF *trans* NITROUS ACID

Method	HO	O-N	N=O	HON	ONO	Torsion
MP2/6-31G(d)	8.6001	2.9125	13.6652	1.3398	2.6625	0.2499
scaled	7.5319	2.1299	12.3437	1.1593	2.4159	0.2065
B3LYP/6-31G(d)	8.5974	2.7495	20.2231	1.3169	2.3439	0.2461
scaled	7.5296	2.010	18.2675	1.1395	2.1268	0.2034
B ₃ LYP/6-31+G(d)	8.5461	2.4815	20.7024	1.2919	2.4347	0.2397
scaled	7.4846	1.8147	18.7004	1.1178	2.2092	0.1981

^aThe scale factor of calculated force constants for O-H, N-O, N=O, (HON), (ONO) and torsion are 0.8758, 0.7313, 0.9033, 0.8653, 0.9074 and 0.8267, respectively [Ref. 31].

Deeley and Mills [31], the scaled results were introduced in Tables 6 and 7. The minimum root mean square was found to be 180.3, 53.09, 29.20 and 27.16 cm⁻¹ for *trans* nitrous acid by PM3, MP2/6-31G (d), B3LYP/6-31+G(d) and B3LY/6-31G(d), respectively.

Conclusion

This work involves the theoretical calculation of the force constant of *trans* nitrous acid by Wilson's methods of F&G matrices, root mean square (rms) has been used as measuring criteria, rms of nitrous acid is 0.512 cm⁻¹. This method is practicable and gives us better results for the calculation of vibrational frequency in the case of small molecules.

REFERENCES

- E.B. Wilson, J.C. Decius and P.C. Cross, *Molecular Vibrations*, McGraw Hill, London (1955).
- E.B. Wilson, *J. Chem. Phys.*, **9**, 76 (1941).
- F.A. Cotton, *Chemical Application of Group Theory*, John Wiley & Sons, New York, edn 2 (1971).
- G. Turrell, *Infrared and Raman Spectra of Crystals*, Academic Press, London (1972).
- D.M. Seeger, C. Korzeniewski and W. Kowalchuk, *J. Phys. Chem.*, **95**, 6871 (1991).
- A.P. Scott and L. Radom, *J. Phys. Chem.*, **100**, 16502 (1996).
- J.M. Coffin and J. Pulay, *J. Phys. Chem.*, **95**, 118 (1991).
- T.P. Hamilton and P. Pulay, *J. Phys. Chem.*, **93**, 2341 (1989).
- E.D. Simandiras, J.E. Rice, T.J. Lee, R.D. Amos and N.C. Handy, *J. Chem. Phys.*, **88**, 3187 (1988).
- G. Fogarasi and P. Pulay, *J. Mol. Struct.*, **39**, 275 (1977).
- E.F. Healy and A. Holder, *J. Mol. Struct.*, **281**, 141 (1993).
- J.A. Pople, H.B. Schlegel, R. Krishnan, D.J. Defrees, J.S. Binkley, M.J. Frisch, R.A. Whiteside, R.F. Hout and W.J. Hehre, *Int. J. Quantum Chem. Quantum Chem. Symp.*, **15**, 269 (1981).
- R.F. Hout, B.A. Levi and W.J. Hehre, *J. Comput. Chem.*, **3**, 234 (1982).
- L.A. Curtiss, K. Raghavachari, G.W. Trucks and J.A. Pople, *J. Chem. Phys.*, **94**, 7221 (1991).
- G. Rauhut and P. Pulay, *J. Am. Chem. Soc.*, **117**, 4167 (1995).
- B.G. Johnson, P.M.W. Gill and J.A. Pople, *J. Chem. Phys.*, **98**, 5612 (1993).
- G. Rauhut and R. Pulay, *J. Phys. Chem.*, **99**, 3093 (1995).
- J.W. Finley and P.J. Stephens, *J. Mol. Struct.*, **357**, 225 (1995).
- D.J. Finnigan, A.P. Cox, A.H. Brittain and J.G. Smith, *J. Chem. Soc., Faraday Trans. II*, **68**, 548 (1972).
- S. Skaarup and J.E. Boggs, *J. Mol. Struct.*, **30**, 389 (1976).
- R. Varma and R.F. Curl, *J. Phys. Chem.*, **80**, 402 (1976).
- A. Palm, *J. Chem. Phys.*, **26**, 855 (1957).
- G.E. McGraw, D.L. Bernitt and L.C. Histatsune, *J. Chem. Phys.*, **45**, 1392 (1966).
- P. Ling, A.I. Boldyrev, J. Simons and C.A. Wight, *J. Am. Chem. Soc.*, **120**, 12327 (1998).
- F. Glauco, G.A. Bauerfeldt and C.D.S. Edilson, *J. Braz. Chem. Soc.*, **16**, 190 (2005).
- H. Hirohara, M. Nakayama and N. Ise, *J. Chem. Soc., Faraday Trans. 1*, **68**, 58 (1972).
- C.C. Costain and J.M. Dowling, *J. Chem. Phys.*, **32**, 158 (1960).
- The MathWorks Inc. MATLAB 7.0 (R14SP2), The MathWorks Inc. (2005).
- J.J.P. Stewart, MOPAC 2007, Stewart Computational Chemistry, Version 8.211W (2007); web:HTTP://OpenMOPAC.net.
- M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski and D.J. Fox, Gaussian 09 Program, Revision A.02, Gaussian, Inc., Wallingford CT (2009).
- C.M. Deeley and I.M. Mills, *Mol. Phys.*, **54**, 23 (1985).