Journal of Molecular Structure: THEOCHEM 725 (2005) 157–161

THEO CHEM

www.elsevier.com/locate/theochem

Ab initio and density functional calculations of the structures and vibrational spectra of formaldoxime

Yunusa Umar*, Tijani Jimoh, M.A. Morsy

Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

Received 21 January 2005; revised 14 March 2005; accepted 14 March 2005
Available online 13 June 2005

Abstract

Molecular structure and vibrational frequencies of formaldoxime, $CH_2{=}NOH$, have been investigated with ab initio and density functional theory (DFT) methods. The molecular geometries for all the possible conformers of the molecule were optimized using DFT-B3LYP, DFT-BLYP and MP2 applying the standard 6-311+G** basis set. From the calculations, the molecule was predicted to exit predominantly in *trans* conformation with the *trans–cis* rotational barrier of about 9.2–9.7 kcal/mol depending on the level of theory applied. The vibrational frequencies and the corresponding vibrational assignments of formaldoxime in C_s symmetry were examined theoretically and the calculated infrared and Raman spectra of the molecule in the *trans* conformation were plotted. Observed frequencies for normal modes were compared with those calculated from normal mode coordinate analysis carried out on the basis of ab initio and DFT force fields using the standard 6-311+G** basis set of the theoretical optimized geometry. Theoretical IR intensities and Raman activities are reported.

Keywords: Density functional method; Ab initio; Vibrational frequencies; Infrared spectra; Raman spectra; Formaldoxime; formaldehyde oxime.

1. Introduction

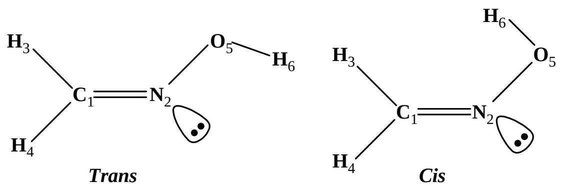
Formaldoxime $CH_2{=}NOH$, the simplest member of the oxime family and a rare example of small molecules containing C=N bond was first reported in the literature in 1898 [1]. It has been extensively used as analytical reagent [2–4] and more recently in polymer synthesis [5]. $CH_2{=}NOH$ have been shown to have planar structure with C_s symmetry. The vibrational spectroscopy of formaldoxime has been investigated in some details [6–10]. Califano and Luttke [6] studied the infrared spectrum of formaldoxime in the vapor phase and concluded that the *cis* conformer is more stable. Earlier and subsequent infrared and microwave spectrum studies arrived to the opposite conclusion [7–10]. There have been several theoretical [11–20] molecular orbital calculations of formaldoxime. Most of these calculations were carried out with experimental, assumed or standard geometries, and were concerned largely with the individual stable isomers, associated conformation problems and hydrogen shift rearrangement. However, there is no analysis of the vibration modes and vibrational frequencies employing density functional theory (DFT) methods especially for different conformations of the same molecule. Modern vibrational spectroscopy has proven to be an exceptional technique for solving chemistry problems.

In this study, molecular geometry, infrared and Raman spectra of $CH_2{=}NOH$ were investigated using the GAUSSIAN 98 program package [21] and compared against experimental molecular geometry and vibrational data. The energies of the possible conformers and the transition states of the molecules were optimized using ab initio and DFT methods. In DFT method, Beck's gradient-corrected exchange functional combined with Lee–Yang–Parr gradient-corrected exchange functional (BLYP) and Becke's three-parameter exchange functional combined with Lee–Yang–Parr correlation functional (B3LYP) methods were employed using the standard 6-311+G** basis set. The same basis set was used for second-order Møller–Plesset (MP2) perturbation theory. From the data, the relative conformational stability and the barrier to internal rotation were determined. Furthermore, vibrational frequencies were also computed at all the three levels and a complete

---

* Corresponding author. Tel.: +966 50 2045518; fax: +966 3 8604277.
E-mail address: uyunusa@kfupm.edu.sa (Y. Umar).

0166-1280/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.theochem.2005.03.036



Scheme 1. Atom numbering for formaldoxime in the *trans* and *cis* form.

assignment of the fundamental vibrational modes was done on the basis of comparison between the calculated and experimental results.

2. Computational methods

GAUSSIAN 98 program package was used to optimize the structure, predict energies and dipole moment and calculate the vibrational frequencies for formaldoxime, $CH_2=NOH$ in its possible structures (Scheme 1). Calculations were performed at DFT-B3LYP, DFT-BLYP and MP2 levels of theory. The standard 6-311+G** basis set was used to carryout the calculations utilizing the C_s symmetry of $CH_2=NOH$. Some of the optimized bond lengths and bond angles of formaldoxime are listed in Table 1; the reported experimental molecular parameters are also listed therein. The optimized geometries of *trans* conformer determined at all the three levels of theory are in good agreement with reported experimental data obtained by microwave spectroscopy [9].

To study different conformations of the molecule, potential energy scans (PES) for the internal rotation about the O–N single bond was performed at all the three levels of theory. Torsional angle ϕ (CN–OH) was varied in steps of 15° between $\phi = 0°$ (*cis* position, where O–H bond eclipses the C=N bond) to $\phi = 180°$ (*trans* position, where the O–H bond is *anti* to the C=N bond). The saddle points were determined and full geometry optimization was carried out at the transition state. In addition, full geometry optimization at each of the fixed CN–OH torsional angle (ϕ) of 15, 30, 45, 60, 75, 90, 105, 120, 135, 150, and 165° were carried out at B3LYP/6-311+G**, BLYP/6-311+G** and MP2/6-311+G** levels of calculations. The asymmetric potential functions for the internal rotation in the molecules are presented in Fig. 1.

HyperChem™ [22] operating on MS-Windows was used to display all the vibrational modes associated with each calculated spectral line following a procedure previously reported [23]. The computed IR spectrum was produced from Gaussian output files using freqChk utilities provided in the GAUSSIAN 98W package.

3. Results and discussion

The geometry parameters optimized at MP2, DFT-B3LYP and DFT-BLYP levels of theory for the *cis* and *trans* conformers of formaldoxime are presented in Table 1 along with the reported experimental data. Standard basis set 6-311+G** was utilized in all calculations. Compared

Table 1

Optimized structural parameters[a], total dipole moment, and rotational constants at B3LYP/6311+G**, BLYP/6311+G** and MP2/6311+G** levels for the *trans* and *cis* conformers of formaldoxime

Parameter	B3LYP/6311+G**		BLYP/6311+G**		MP2/6311+G**		Expt[b]
	trans	*cis*	*trans*	*cis*	*trans*	*cis*	
Bond length (Å)							
$r(C_1–H_4)$	1.089	1.095	1.096	1.102	1.089	1.095	1.085
$r(C_1–H_3)$	1.084	1.084	1.090	1.090	1.083	1.083	1.086
$r(C_1=N_2)$	1.269	1.269	1.281	1.283	1.282	1.283	1.276
$r(N_2–O_5)$	1.401	1.380	1.434	1.406	1.397	1.379	1.408
$r(O_5–H_6)$	0.964	0.975	0.974	0.988	0.962	0.973	0.956
Bond angle (degree)							
$H_4C_1H_3$	120.6	119.3	120.5	119.3	121.5	120.0	122.7
$H_4C_1N_2$	122.9	123.6	123.4	124.0	122.5	123.3	121.8
$H_3C_1N_2$	111.5	117.1	116.1	116.7	116.0	116.6	115.6
$C_1N_2O_5$	111.5	116.8	111.0	116.5	110.7	115.7	110.2
$N_2O_5H_6$	103.2	109.5	102.2	109.1	102.5	108.2	102.7
$C_1N_2O_5H_6$	180.0	0.0	180.0	0.0	180.0	0.0	
Dipole moment (Debye)							
μ_t	0.35	3.32	0.38	3.24	0.37	3.38	0.44[c]
Rotational constant (GHz)							
A	69.55	66.64	66.95	64.76	67.98	64.99	67.68
B	11.81	11.95	11.50	11.64	11.88	12.00	11.86
C	10.10	10.13	9.81	9.87	10.11	10.13	10.08

[a] Atom numbering is shown in Fig. 1.

[b] Experimental values taken from Ref. [9].

[c] Experimental value taken from Ref. [8].

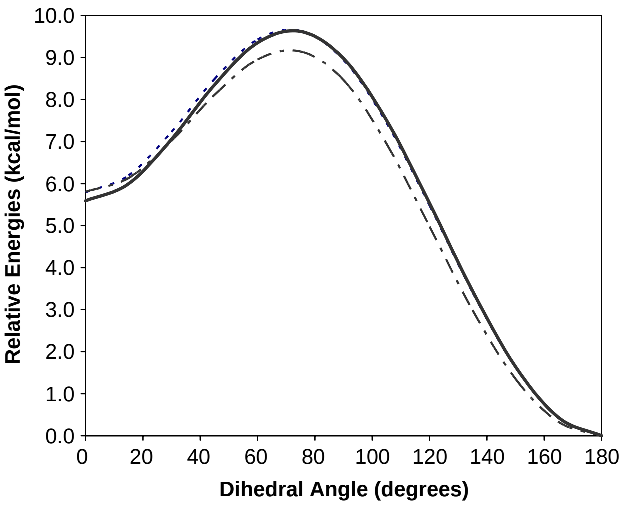


Fig. 1. Torsional potential curves of formaldoxime as a function of dihedral angle (ϕ) computed at B3LYP/6-311+G** (dotted line), BLYP/6-311+G** (solid line) and MP2/ 6-311+G** (dashed line).

with the available experimental values [9], B3LYP/6-311+G** showed the best agreement between the calculated bond lengths of the *trans* conformer and experimental values. The bond angles obtained by the MP2/6-311+G** of *trans* conformer agree well with the experimental values. Our computed geometry optimization indicates that the bond lengths calculated at BLYP/6-311+G** are slightly longer than those of the corresponding B3LYP/6-311+G**. The geometric parameters related with N and O atoms have shown marked differences between the *trans* and *cis* conformers due to lone pair electrons.

Total dipole moment obtained from geometry optimization of *trans* conformer at all the three levels of calculations (DFT-B3LYP=0.35 D, DFT-BLYP=0.38 D and MP2=0.37 D) were found to be relatively consistent with experimental value (0.44 D) and smaller than those predicted from geometry optimization of *cis* conformer (DFT-B3LYP=3.32 D and DFT-BLYP=3.24 D and MP2=3.38 D). This fact alone is strong evidence for *trans* conformer, as bond moments calculated indicate small dipole moments for *trans* and large dipole moments for *cis*. The unusual dipole moment for *trans* (for a molecule containing polar OH) is due to cancellation of bond dipole associated with polar end of the molecule. The calculated rotational constants R_A, R_B, and R_C for the two conformers are summarized in Table 1. These computed rotational constants agree fairly well with the reported experimental values obtained by microwave spectroscopy [8].

The optimized structural parameters were used to compute the vibrational frequencies of formaldoxime at MP2, DFT-B3LYP and DFT-BLYP levels of theory. Standard basis set 6-311+G** was utilized in all calculations. Table 2 presents the calculated vibrational frequencies for the *trans* conformer of formaldoxime computed at the DFT-B3LYP, DFT-BLYP and MP2 levels of theory. These calculations result in 12 IR and Raman active fundamental vibrations that belong to only two irreducible representations of the C_s point group, nine belonging to A' (in-plane) modes and three to A'' (out-of-plane) modes. The calculated vibrational frequencies of the *cis* conformer and the transition state are presented in Tables S1 and S2, respectively, of the supporting material. The calculated vibrational infrared and Raman spectra of the *trans* formaldoxime at DFT-BLYP/6-311+G** are shown in Figs. 2 and 3.

The normal modes associated with individual vibrations are graphically displayed using HyperChem vibrational spectrum with active IR vector utilizing FrqChk utility provided with the GAUSSIAN 98 to prepare the checkpoint file. Combining the visual inspection of the vector rendering of

Table 2

Fundamental vibrational frequencies (cm^{-1}) of *trans* formaldoxime calculated at the DFT (B3LYP), DFT (BLYP) and MP2 level of theory using the standard 6-311+G** basis set

Sym.	No.	DFT-B3LYP/6-311+G**			DFT-BLYP/6-311+G**			MP2/6-311+G**			Assignment	Expt[a]. freq.
		Calc. freq.	IR[b] intensity	Raman activity[c]	Calc. freq.	IR[b] intensity	Raman activity[c]	Calc. freq.	IR[b] intensity	Raman activity[c]		
A'	ν_1	3829	98.0	86.6	3678	77.6	94.1	3880	103.0	76.4	O–H stretch	3646
	ν_2	3222	3.3	71.2	3138	4.1	80.5	3296	1.9	58.6	CH_2 stretch, ass.	3106
	ν_3	3095	5.8	109.3	3013	7.7	121.4	3155	3.3	104.8	CH_2 stretch, sym.	2969
	ν_4	1709	5.9	15.2	1625	7.6	10.6	1671	4.8	5.6	C=N stretch	1647
	ν_5	1447	13.8	6.2	1402	9.9	7.1	1463	10.3	5.3	CH_2 scissor	1410
	ν_6	1346	90.2	14.8	1294	85.5	15.6	1351	86.5	10.7	O–H bend	1318
	ν_7	1177	9.2	0.7	1131	6.6	0.6	1189	6.3	0.5	CH_2 rock	1166
	ν_8	913	131.4	9.0	823	128.9	10.6	939	107.4	5.4	N–O stretch	888
	ν_9	536	6.7	2.6	514	6.6	3.1	537	6.4	2.2	C–NO deformation	530
A''	ν_{10}	984	38.9	1.7	931	38.8	1.6	967	41.9	1.0	CH_2 deformation I	950
	ν_{11}	798	6.6	1.8	767	9.6	1.6	800	5.6	2.0	CH_2 deformation II	769
	ν_{12}	425	148.6	0.3	421	135.9	0.4	370	148.2	0.2	O–H torsion	400

[a] Units of IR intensities are km/mol.

[b] Units of Raman activities are Å^4/a.m.u.

[c] Experimental values taken from Ref. [10].

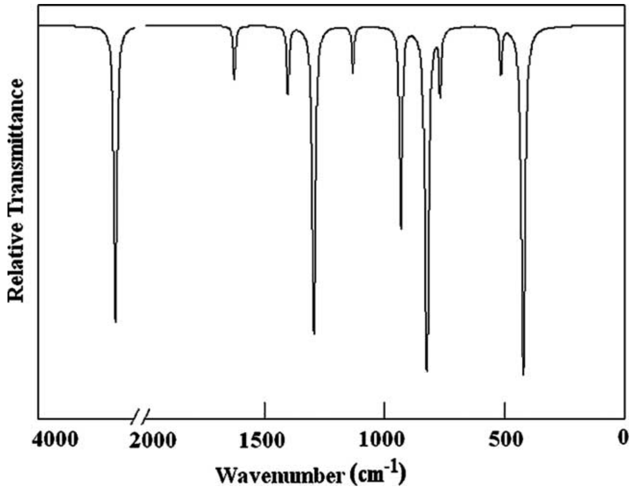


Fig. 2. Theoretical vibrational infrared spectrum of the *trans* formaldoxime computed at the DFT-BLYP/6311+G** level.

HyperChem program, infrared band intensities and Raman line activities, with the experimental reported results, complete vibrational frequency assignments were made with high degree of confidence. Each vibrational mode was assigned to one of 10 types of motion (O–H stretch, CH_2 stretch, C=N stretch, CH_2 scissor, O–H bend, CH_2 rock, N–O stretch, C=N–O deformation, CH_2 deformation and O–H torsional). The predicted vibrational frequencies indicate that DFT method especially BLYP reproduce experimental vibrational frequencies with higher accuracy than the MP2 calculations. This is in good agreement with previous studies [24].

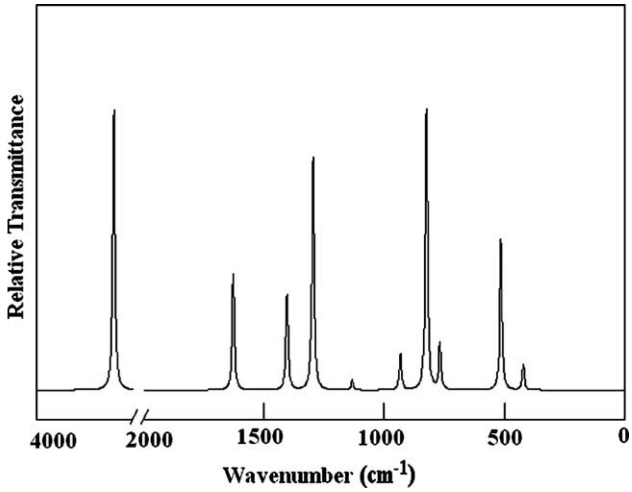


Fig. 3. Theoretical vibrational Raman spectrum of the *trans* formaldoxime computed at the DFT-BLYP/6311+G** level.

Table 3
Computed total energies (hartrees) and/or zero-point corrections (kcal/mol), and relative energy and rotational barriers (kcal/mol) in formaldoxime calculated at DFT-B3LYP, DFT-BLYP and MP2 levels using 6-311+G** basis set.

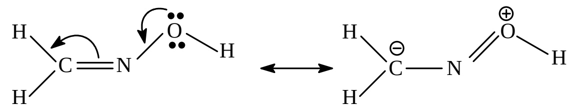
Level/parameter	DFT-B3LYP	DFT-BLYP	MP2
Total energy			
cis	−169.862476	−169.826337	−169.410990
trans	−169.871709	−169.835245	−169.420241
TS[a]	−169.856304	−169.819885	−169.405625
Relative Energy	5.79	5.59	5.81
cis–trans barrier	3.87	4.05	3.37
trans–cis barrier	9.67	9.64	9.17
Zero-point correction			
cis	27.50	26.39	27.74
trans	27.85	26.79	28.05
TS	26.93	25.85	27.25
Corrected relative energy	5.45	5.20	5.50
Corrected *cis–trans* barrier	3.30	3.50	2.88
Corrected *trans–cis* barrier	8.75	8.70	8.38

[a] Transition state energy, dihedral angle at the transition state was found to be 71.3, 72.3 and 71.3° at B3LYP, BLYP and MP2 levels, respectively.

Computed total energies of the two conformers and the transition state of the molecules calculated at MP2, B3LYP and BLYP are presented in Table 3. Relative energies, corrected relative energies and rotational barriers are also presented therein. The *trans* conformer was found to be more stable than *cis* conformer by 5.44 kcal/mol at DFT-B3LYP, 5.20 kcal/mol at DFT-BLYP level and 5.50 kcal/mol at DFT-BLYP. The observation that the *trans* conformer is more stable than *cis* is consistent with reported infrared and microwave spectroscopy [7–10]. The energy difference has been previously calculated [12,13] using standard geometries with the STO-3G and 4-31G basis sets, yielding values of 5.74 and 10.76 kcal/mol, respectively, in favor of *trans* conformer, whereas calculations [14] using floating spherical Gaussian orbital (FSGO) produced an energy difference of 6.93 kcal/mol.

From full-energy optimization, the molecule was predicted to have planar geometry with methylene group tilted towards the lone pair of the nitrogen atom to which it is bonded. The pronounced conjugation between the C=C and the C=O moieties in propenals which considerably hinders internal rotation in these compounds was reported to be responsible for stability of their planar structures [25,26]. Thus, the planarity in formaldoxime will be favored by the resonance structure shown in Scheme 2.

Because of the resonance, the C–N bond length predicted at DFT-B3LYP, DFT-BLYP and MP2 levels (see Table 1) are longer than pure C–N double bond (1.265 Å) and the N–O bond lengths are shorter than pure N–O single bond (1.44 Å) [9,27]. Similarly, the *trans* conformer was found to



Scheme 2. Resonance structure of *trans* formaldoxime.

be the minima in the potential energy surface with *trans–cis* internal rotational barrier of about 9.2–9.7 kcal/mol depending on the level of theory applied. This high rotational barrier is as a result of the possible conjugation where the N–O single bond has some π-character as depicted in Scheme 2.

4. Conclusions and summary

Ab initio and DFT geometry optimization have been performed for the possible conformers and transition state of formaldoxime using GAUSSIAN 98 package. The potential energy curves were obtained for the CN–OH rotational angle at MP2/6-311+G**, B3LYP/6-311+G** and BLYP/6-311+G**. The *trans* conformer was found to have lower energy and the geometry compared well with experimental values determined by microwave spectroscopy. The normal modes and corresponding vibrational assignment of formaldoxime were theoretically examined. A complete assignment of the fundamental vibrational modes is proposed based on the HyperChem™ visualization program and experimental results. Theoretical infrared and Raman spectra are reported. Density functional methods yield a good description of the vibrational modes of formaldoxime. Thus, it seems that this method is a promising approach and sufficient enough for reliable prediction of frequency and geometry optimization of similar molecular systems.

Acknowledgements

The support of King Fahd University of Petroleum and Minerals is gratefully acknowledged.

References

[1] W.R. Dunstan, A.L. Bossi, J. Chem. Soc. 73 (1898) 353.
[2] B. Chiswell, K.R. O'Halloran, Talanta 38 (1991) 641.
[3] A.P. Argekar, A.K. Shelty, Anal. Sci. 13 (1997) 131.
[4] M. Dogutan, H. Filik, R. Apak, Anal. Chim. Acta 485 (2003) 205.
[5] D. Dallas, A.B. Padias, H.K. Hall, J. Polym. Sci. Part A: Polym. Chem. 40B (2001) 181.
[6] S. Califano, W. Luttke, Z. Phys. Chem. 6 (1956) 83.
[7] L.R. Zumwalt, R.M. Badger, J. Chem. Phys. 7 (1939) 235.
[8] I.N. Levine, J. Mol. Spectrosc. 8 (1962) 276.
[9] I.N. Levine, J. Chem. Phys. 38 (1963) 2326.
[10] A. Azman, D. Hazi, J. Kidric, B. Orel, C. Trampuz, Spectrochim. Acta 27A (1971) 2499.
[11] M.A. Robb, I.G. Csizmadia, J. Chem. Phys. 50 (1969) 1819.
[12] L. Random, W.J. Hehre, J.A. Pople, J. Chem. Soc. A 1971; 2299.
[13] L. Random, W.J. Hehre, J.A. Pople, J. Am. Chem. Soc. 93 (1971) 289.
[14] W.F. Hwang, H.A. Kuska, J. Mol. Struct. 48 (1978) 239.
[15] P.A. Adney, W.J. Bouma, L. Radom, W.R. Rodwell, J. Am. Chem. Soc. 102 (1980) 4069.
[16] K. Akagi, Y. Tanabe, T. Yamabe, J. Mol. Struct. 102 (1/2) (1983) 103.
[17] D.M. Schnur, D.R. Dalton, J. Org. Chem. 53 (1988) 3313.
[18] A.H. Otto, J. Mol. Struct. (THEOCHEM) 235 (1/2) (1991) 489.
[19] P. Kolandaivel, K. Senthilkumar, J. Mol. Struct. (THEOCHEM) 535 (2001) 61.
[20] J.A. Long, N.J. Harris, K. Lammertsma, J. Org. Chemistry 66 (2001) 6762.
[21] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, Jr., 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. Petersson, 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. Nanayakkara, C. Gonzalez, 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.6, Gaussian, Inc., Pittsburgh PA, 1998.
[22] HyperChem™ version 5.01, Molecular Modeling System, Hypercube, Waterloo, Ont., Canada, 1996.
[23] A. Suwaiyan, M.A. Morsy, Spectrochim. Acta Part A 53 (1997) 575.
[24] M.A. Morsy, M.A. Al-Khalid, A. Suwaiyan, J. Phys. Chem. A 106 (2002) 9196.
[25] J.R. Durig, G.A. Guirgis, H.V. Phan, J. Raman Spectrosc. 21 (1990) 359.
[26] J.R. Durig, A.Q. McArver, H.V. Phan,, G.A. Guirgis, J. Chem. Phys. 95 (1991) 539.
[27] L. Pauling, The Nature of the Chemical Bond, Cornell University Press, Ithaca, NY, 1960. pp. 228–229.