Density functional and post Hartree–Fock equilibrium geometries, potential energy surface and vibrational frequencies for methylamine

Gábor I. Csonka [a], Lajos Sztraka [b]

[a] *Department of Inorganic Chemistry, Technical University of Budapest, 1521 Budapest, Hungary*
[b] *Department of Physical Chemistry, Technical University of Budapest, 1521 Budapest, Hungary*

Received 23 November 1994; in final form 22 December 1994

Abstract

The equilibrium structure, the potential energy surface and the infrared harmonic frequencies are determined by using two generalized gradient approximation density functional methods for methylamine. The results are compared to those of a second-order Møller–Plesset and coupled cluster calculations. The DFT methods predict correctly the equilibrium geometry, the inversion energy barrier and the infrared spectra. The B-P86 method show better agreement with the experiment than the MP2 or CCD methods.

1. Introduction

Generalized gradient approximation density functional (GGA-DFT) and ab initio MO calculations are useful tools for predicting molecular geometries and the potential energy hypersurfaces (PEH). The methylamine molecule is rich in structural features that can be studied experimentally and small enough for very high level calculations. In methylamine two large amplitude internal motions, the inversion of the amino group and the internal rotation along the C–N bond, are strongly coupled with each other and with the pure rotation of molecule resulting in complicated infrared (IR) and microwave (MW) spectra. Thus the assignment of these spectra and the analysis of the large amplitude motions are difficult to achieve. One of the difficulties is that the determination of the PEH from the high resolution spectra

requires a precise knowledge of the molecular geometry at any point of the hypersurface.

The potential function and especially the barrier to inversion was only roughly estimated in early studies [1,2] because of the serious simplifications in the theoretical model applied in those studies. Kręglewski [3] tried to solve this problem by introducing a Hougen–Bunker–Johns-type [4] rigid inversion–internal rotation–rotation Hamiltonian. The shape of the potential surface was calculated without relaxing other geometrical parameters. To overcome the difficulties arising from the rigid model Kręglewski introduced later a semirigid model [5] in which bond lengths and angles may change as function of the inversion coordinate. However, the semirigid approximation applied in that paper used some unjustifiable approximations. For example a simple linear, quadratic and quartic dependence of the geo-

metrical parameters on the inversion coordinate was assumed.

In our previous paper the inversion potential function of methylamine was determined from MW and IR data with parallel determination of geometries of ground and excited states using a rigid model [6]. As the geometry was fitted to the experimental rotational coefficients, the averaging effect of inversion was taken into consideration. The rigid model, in which some of the bond lengths and bond angles were kept constant, introduced a considerable uncertainty into the values of the geometrical averages. It is clear that it is not possible to determine the equilibrium geometries of a sufficiently flexible molecule from the high resolution spectra or from the electron diffraction data alone, since these methods yield an average structure.

The reliable ab initio and GGA-DFT calculations may help to overcome this difficulty because the changes in structural parameters caused by the large amplitude movements can be followed. The resulting PEH-geometry functionals can be introduced directly into the rotation–internal rotation–inversion Hamiltonian. The average of geometrical parameters can also be calculated straightforwardly from these functionals and this way the theoretical results can be compared to experimental data. In this Letter, we use several different quantumchemical methods, to check the consistency of the theoretical predictions. We also give the calculated inversion and rotational barriers, rotational constants, the harmonic vibrational frequencies and rotational constants and compare them to the experimental results.

2. Computational methods

The geometry of methylamine was fully or partially optimized at the selected points of the potential energy surface (PES). The triple-split-valence plus polarization 6-311G(d), and G(d, p) basis sets [7] were used in the present calculations.

We use these basis sets with the promising functionals of Becke [8,9] (B and B3) and Perdew [10] (P86). The combinations of the functionals were as follows:

(i) B-P86 or Becke–Perdew method, in which Becke's exchange functional [8] is combined with Perdew's correlation functional [10].

(ii) B3-P86 is a hybrid method. It is a linear combination of various exchange and correlational functionals in the form

$$AE_x[HF] + (1 - A)E_x[S] + BE_x[B]$$
$$+ E_c[VWN] + CE_c[P86].$$

where $E_x[HF]$, $E_x[S]$ and $E_x[B]$ are the HF, Slater and Becke exchange functionals; and $E_c[VWN]$ and $E_c[P86]$ are the Vosko, Wilk and Nussair [11] and Perdew correlation functionals [10], respectively. Note that $E_x[B]$ is a gradient correction to the LSDA for exchange and $E_c[P86]$ is a gradient correction for correlation. The constants A, B and C are those determined by Becke by fitting heats of formation ($A = 0.2$, $B = 0.72$, $C = 0.81$) [9]. Note that Becke used the Perdew–Wang 1991 (PW91) functional instead of P86 [9].

GAUSSIAN 92/DFT [12] uses numerical quadrature to evaluate the DFT integrals. The quadrature scheme is defined by the number of points in radial and angular directions. The geometries were optimized first with a normal grid (50 radial shells, 194 angular points per shell, pruned to about 3000 points per atom). We performed several calculations with a finer grid (75 radial shells, 302 angular points per shell, pruned to about 7000 points per atom). The latter has considerably better numerical accuracy and rotational invariance properties than the normal grid. The DFT minima were checked by frequency analysis.

We also calculated the molecular properties with single reference correlated theories, with many-body perturbation theory (MBPT) using Møller–Plesset partition [13] to second order (MP2). Geometries were also optimized at the CCD level of coupled-cluster theory [14]. Single point energy calculations at CCD equilibrium geometries up to fourth order MBPT (MP4SDQ) and to CCSD(T) level of theory have been performed as well to study the energetics. In each calculation the atomic core was frozen. The harmonic frequencies are calculated by analytical second differentiation at HF, DFT and MP2 levels of theory. In CCD calculations the harmonic frequencies were calculated by numerical differentiation of analytical gradients.

The ab initio calculations were carried out using the GAUSSIAN 92/DFT [11] computer program on Silicon Graphics workstations.

3. Results and discussion

The HF equilibrium geometry for methylamine was already published in the literature [15]. It was found that the HF/6-31G(d) equilibrium geometry is in reasonable agreement with the experimental results, and its most important deficiency is the too short CN bond length (145.34 pm). This deficiency is also present in the HF/6-31G(d, p) results [15,16]. Xie et al. [17] pointed out that the HF method supplemented with large basis set (e.g., QZ + 2P + F) did not provide significantly different C–N distance. These results show that the HF results are converged for methylamine at HF/6-31G(d) level of theory and the extension of the basis set will not lead to different results. The improper treatment of electron correlation causes bond lengths to be underestimated in HF calculations supplemented with extended basis sets. In these type of calculations the electron–electron repulsion terms are underestimated, and the electrons tends to move too close to each other. The stronger Coulombic attraction between electrons and nuclei results compact bonds.

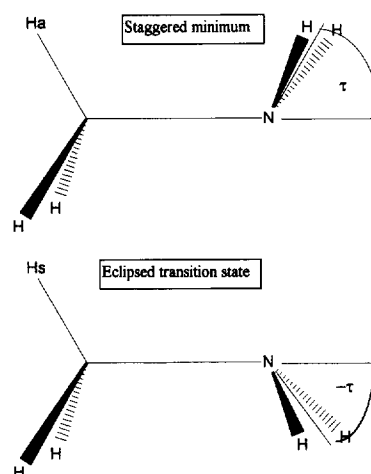The inclusion of the electron correlation lengthens the C–N bond and provides a better agreement with

Fig. 1. The staggered minimum and the eclipsed conformations for methylamine. τ denotes the angle between the C–N bond and the NH_2 plane. H_a or H_s denotes the H in anti or syn position relative to the N lone pair, respectively.

the experiment. The MP2 and CCD results in Table 1 provide a bond lengthening similar to each other. (For the notations used in Table 1 see Fig. 1.) It is known that the expensive CCD method supplemented with polarized triple split valence basis set

Table 1
Calculated and experimental ground state geometries and total energies for staggered C_s conformation of methylamine ($\lambda = 0$, local minimum)

Geometrical parameter [a]	MP2/ 6-311G(d)	MP2/ 6-311G(d, p)	CCD/ 6-311G(d)	B3-P86/ 6-311G(d)	B-P86/ 6-31G	B-P86/ 6-31G(d5)	B-P86/ 6-31G(d)	B-P86/ 6-31G(d)	Exp. MW [b]	ED + MW [c]
r(CN)	146.41	146.48	146.57	145.62	146.58	147.18	147.17	147.19	147.14	147.1(3)
r(CH$_a$)	109.90	109.99	110.18	110.16	111.77	111.50	111.50	111.20	109.87	110.1(3)
r(CH)	109.15	109.27	109.46	109.28	110.45	110.47	110.47	110.20	109.87	110.1(3)
r(NH)	101.18	101.41	101.31	101.34	102.09	102.81	102.81	102.47	100.96	101.9(6)
$\angle$NCH$_a$	115.24	115.25	115.09	115.76	116.19	116.37	116.37	116.13	113.90	
$\angle$NCH	108.99	109.08	109.05	109.29	109.30	109.00	108.99	109.11		
$\angle$HCH	107.23	107.23	107.23	106.76	106.92	107.03	107.03	106.78	108.00	108.4(5)
$\angle$CNH	109.68	109.68	109.58	110.09	114.94	109.04	108.98	109.35	110.27	111.5(7)
$\angle$HNH	106.87	105.77	106.66	106.43	111.99	105.24	105.17	105.75	107.131	06.0(6)
$\angle \epsilon$ [d]	4.17	4.11	4.03	4.31	4.59	4.92	4.92	4.68	2.93	2.97
$\angle \tau$ [e]	55.58	56.83	55.85	55.00	41.04	57.50	57.62	56.71	54.32	
energy [d]	−95.54570	−95.58746	−95.57095	−96.20363	−95.82303	−95.84669	−95.84857	−95.87372		

[a] Bond length in pm, bond angle in deg. H_a denotes the H in the anti position relative to the nitrogen lone pair.
[b] Ref. [18]. [c] Ref. [19].
[d] $\epsilon = \frac{2}{3}(NCH_t - NCH)$ in the calculations. The experimental ϵ value is defined as the angle between the symmetry axis of methyl group and the CN bond.
[e] τ is the equilibrium angle between the NH_2 plane and the CN bond (Fig. 1).
[d] Total energy (hartree).

Table 2
Calculated geometries for methylamine with planar NH_2 ($\lambda = 2$, internal rotation inversion transition state)

Geometrical parameter [a]	MP2/ 6-311G(d)	MP2/ 6-311G(d, p)	CCD/ 6-311G(d)	B3-P86/ 6-311G(d)	B-P86/ 6-311G(d)
r(CN)	143.77	143.74	143.95	143.05	144.06
r(CH$_s$)	109.97	110.09	110.25	110.26	111.38
r(CH)	109.34	109.45	109.65	109.47	110.43
r(NH)	99.75	99.85	99.80	99.93	100.82
∠NCH$_s$	114.33	114.41	114.23	114.65	114.91
∠NCH	110.21	110.26	110.22	110.56	110.58
∠HCH	106.60	106.60	106.61	106.25	106.20
∠CNH	121.13	121.00	121.30	121.27	121.26
∠HNH	117.74	118.00	117.40	117.49	117.48
∠τ [b]	0.00	0.00	0.00	0.00	0.00
energy [c]	− 95.53579	− 95.57696	− 95.56062	− 96.19524	− 95.86480

[a] Bond length in pm, bond angle in deg. H$_s$ denotes the H in the orthogonal position relative to the NH_2 plane.
[b] τ is the angle between the NH_2 plane and the CN bond (Fig. 1).
[c] Total energy (hartree).

gives excellent geometry for closed shell molecules containing single bonds. The extension of the 6-311G(d) basis set with the p polarization functions on the hydrogen atoms influence only slightly the MP2 equilibrium geometry. The C–H and N–H bonds are lengthened about 0.1 pm and the H–N–H bond angle is decreased by 1° (Table 1). The B3-P86 geometry provides too short C–N bond length and the other bond lengths agree well with the MP2 and CCD results. The inclusion of the HF exchange into the B3-P86 functionals provide results close to the

HF results for the C–N bond. The C–N bond length provided by the B-P86/6-31G method agree well with the MP2 and CCD results, however the lack of d-polarization functions on the heavy atoms cause inadequate description of the pyramidality of the NH2 group (see the value of the equilibrium τ in Table 1). The best agreement with the experiment for the C–N bond length is provided by the B-P86 method supplemented with polarized double- and triple-zeta split-valence basis sets. The number of d orbitals (five or six) added to the 6-31G basis set

Table 3
Calculated eclipsed C_s geometries for methylamine ($\lambda = 1$, internal rotation transition state)

Geometrical parameter [a]	MP2/ 6-311G(d)	CCD/ 6-311G(d)	B3-P86/ 6-311G(d)	B-P86/ 6-311G(d)
r(CN)	147.09	147.27	146.34	147.98
r(CH$_s$)	109.28	109.53	109.50	110.46
r(CH)	109.34	109.65	109.44	110.38
r(NH)	100.90	101.02	101.02	102.14
∠NCH$_s$	110.53	110.53	110.91	110.68
∠NCH	111.98	111.97	112.22	112.38
∠HCH	107.05	107.04	106.80	106.83
∠CNH	110.68	110.55	110.30	110.30
∠HNH	107.21	107.00	106.96	106.14
∠τ [b]	− 53.41	− 53.84	− 52.67	− 54.73
energy [c]	− 95.54172	− 95.56708	− 96.19994	− 95.86998

[a] Bond length in pm, bond angle in deg. Hs denotes the H in the syn position relative to the NH_2 lone pair.
[b] τ is the equilibrium angle between the NH_2 plane and the CN bond (Fig. 1).
[c] Total energy (hartree).

does not influence the equilibrium geometry (six d orbitals provide lower energy in Table 1). The B-P86/6-31G(d) results agree well with the experimental and B-P86/6-311G(d) results (Table 1). We repeated the latter calculation with fine grid. The geometry remained unchanged and the energy was lowered by 0.02 mhartree. There was a controversy for the experimental values for the C–N bond length in the early literature. However, the MW [18] and the recent vibrationally corrected electron diffraction (ED) [19] results are in agreement with each other (Table 1). These make the earlier ED estimation [20] for C–N bond length (146.7(2) pm) obsolete. The $\lambda = 0$ in Table 1 denotes the number of the negative eigenvalues of the Hessian for the optimized geometry. Fig. 1 shows the corresponding equilibrium geometry.

The structural parameters for the transition state with planar configuration ($\lambda = 2$, two negative eigenvalues of the Hessian) is shown in Table 2. The C–N bond is about 3 pm shorter in the planar structure than in the equilibrium structure. The calculated geometries are very similar and the GGA-DFT calculations provide satisfactory results. It should be

noted that the B3-P86 method provides the shortest bond lengths. The B-P86 method provides a good agreement with the CCD results. According to the MP2/6-31G(d) results the internal rotational barrier of the planar amino group around the CN bond is 0.8 cm^{-1}, the internal rotation is practically free.

Table 3 shows the calculated geometry of the eclipsed transition state (Fig. 1) with a single negative eigenvalue of the Hessian ($\lambda = 1$). Again the B3-P86 method provides the shortest bond lengths and the B-P86 method provides the longest bond lengths. The latter is closer to the CCD results.

Table 4 shows the calculated internal rotational and the inversion barrier heights in cm^{-1}. Fig. 2 shows the potential energy curve as a function of τ. The calculated internal rotational barriers are somewhat larger than the effective experimental ones. The experimental barrier to internal rotation was determined to 684.1 cm^{-1} from microwave data [18], to 683.7 cm^{-1} from the Q branches of internal rotation [21], and to 718.4 cm^{-1} from the coupled inversion–internal rotation model [5]. The estimated experimental values for the barrier to inversion are 1688 cm^{-1} [22], 2081 cm^{-1} [6] and 1943 cm^{-1} [5].

Table 4
The inversion and internal rotation barrier heights for methylamine calculated with various methods supplemented with 6-311G(d) basis set if not noted

Method	Total energy [a]			Barrier height [b]	
	staggered	eclipsed	$\tau = 0°$	internal rotation	inversion
HF [c]	−95.23101	−95.22726	−95.22169	824	2047
MP2 [c]	−95.54567	−95.54169	−95.53577	874	2173
MP3 [c]	−95.56658	−95.56270	−95.55643	851	2228
MP4D [c]	−95.57442	−95.57052	−95.56401	855	2284
MP4DQ [c]	−95.56999	−95.56612	−95.55974	851	2250
MP4SDQ [c]	−95.57245	−95.56855	−95.56205	855	2282
CCD	−95.57095	−95.56708	−95.56062	850	2267
CCSD [c]	−95.57317	−95.56929	−95.56274	852	2289
CCSD(T) [c]	−95.58216	−95.57821	−95.57139	868	2364
B − P86	−95.87372	−95.86998	−95.86480	820	1957
B3 − P86	−96.20363	−96.19994	−96.19524	810	1841
B-P86/6-311 + G(2df)	−95.88433	−95.88120	−95.87660	688	1697
exp. [d]				684	1688
exp. [e]				718	1943

[a] Energies in hartree. [b] Energies in cm^{-1}.
[c] Calculated with the CCD equilibrium geometry. There is a minor difference relative to the MP2 geometry.
[d] Effective values from Refs. [18,21] for the internal rotation and from Ref. [22] for the inversion.
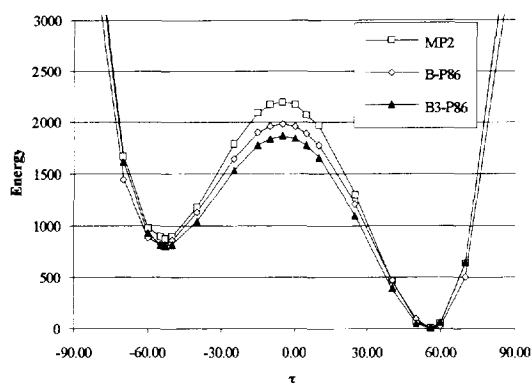[e] Effective value from Ref. [5].

Fig. 2. The τ angle (deg) versus the relative potential energy (cm^{-1}) for methylamine calculated with different methods supplemented with 6-311G(d) basis set.

These values were derived from infrared transitions. The theoretical methods supplemented with the 6-311G(d) basis set support the larger experimental values (these are the more recent values). The extension of the basis set to 6-311 + G(2df) decreases the calculated barrier heights considerably at B-P86 level of theory (Table 4) and these results support the earlier experimental values. It should be noted that

the calculated highest energy point is at $\tau = -5°$ not at $\tau = 0°$ (planar amino group). However, the planar amino group rotates freely, which makes the inversion barrier about 22–25 cm^{-1} lower. The analysis of the high resolution spectra of the ammonia provided that the effective barrier height of the inversion is higher than the true one by 175 cm^{-1} [23]. The latter correction can be derived from the τ dependence of zero point energy. If this holds for the methylamine, the calculated inversion barrier should be below the experimental results. This criteria is fulfilled best by the GGA-DFT methods supplemented with the 6-311G(d) basis set. The B-P86 method provides the best performance.

The correct description of the curvature of the energy hypersurface at the minimum can be controlled by comparison of the calculated and the experimental infrared (IR) spectra. This is a useful test for the theoretical methods. However, the theoretical methods used in this Letter provide the harmonic frequencies, consequently care should be taken during the comparison. The anharmonicity of the experimental frequencies should be taken into consideration. In the IR spectra of methylamine [24,25] the NH_2 wagging and the torsion are anharmonic.

Table 5
The calculated and experimental IR wavenumbers (intensities) and zero point vibrational energies for methylamine

Symm.	Description of mode	HF/6-31G(d)	MP2/6-31G(d) [c]	MP2/6-311G(d)	P86/6-311G(d)	Exp. [a]
a′	NH_2 s-stretch	3730 (1)	3508	3559 (1)	3372 (7)	3360 +
	CH_3 d-stretch	3245 (58)	3155	3135 (40)	2984 (44)	2962 + + + + + +
	CH_3 s-stretch	3158 (99)	3063	3033 (80)	2867 (122)	2820 + + + + + +
	NH_2 scis.	1841 (29)	1745	1750 (36)	1672 (30)	1623 + + + +
	CH_3 d-deform.	1648 (7)	1539	1542 (8)	1466 (9)	1474 + + + +
	CH_3 s-deform.	1608 (4)	1469	1499 (2)	1421 (2)	1430 + + +
	CH_3 rock	1289 (19)	1237	1213 (13)	1149 (7)	1130 + + +
	CN stretch	1148 (18)	1113	1095 (8)	1035 (5)	1044 + + + +
	NH_2 wag.	947 (185)	941	913 (178)	850 (173)	780 + + + + + +
a″	NH_2 a-stretch	3813 (0)	3641	3654 (0)	3451 (3)	3424 +
	CH_3 d-stretch	3282 (51)	3228	3179 (32)	3023 (41)	2985 + + +
	CH_3 d-deform.	1665 (1)	1596	1562 (1)	1489 (4)	1485
	NH_2 twist.	1497 (0)	1405	1393 (0)	1332 (0)	1335 [b]
	CH_3 rock	1052 (0)	915	1000 (0)	962 (0)	972 [b]
	torsion	341 (47)	351	341 (45)	337 (44)	264 + + +
	zero point energy	15124	14453	14433	13706	13544

[a] Ref. [24]. The intensities are denoted by the number of + signs, low intensity peaks are denoted by a dot. The NH_2 wag is anharmonic and it shows an inversion splitting.
[b] Ref. [25]. [c] Ref. [15].

These movements can be related to large amplitude low frequency motions: to the inversion and the internal rotation, respectively.

It is known that HF frequencies are in general too large, the average error is more than 11%. The MP2 method provides uniformly better harmonic frequencies than the HF method. The results in Table 5 show that the BP86 method provide superior agreement with the experiment than the MP2 method. Only the frequencies where anharmonic corrections are expected to be large show considerable difference from the calculated BP86 values, however this is not a deficiency of the theoretical method.

The good equilibrium geometry and barrier heights together with high quality calculated IR spectra lead us to select the B-P86/6-311G(d) method for further studies. We calculated the whole internal rotation–inversion potential energy surface and the functions of the geometrical parameters with this method. To illustrate the performance of the method we show the following example. For the ground state of the methylamine the R_J, R_k, Δ_{as} and ρ effective constants are available from the high resolution MW, millimetre wave and far-IR spectra [26,27]. The R_J is derived from the $J(J+1)$ terms, the R_k is derived from k^2 terms, the Δ_{as} is derived from the off-diagonal elements of the Hamiltonian and the ρ provides the periodicity of the energy levels arising from the internal rotation. The results for these constants are shown in Table 6. The rotational coefficient functions were derived by averaging according to the inversion [6] applying the geometrical data obtained from the B-P86/6-311G(d) calculations. We also applied a Coriolis correction [19] to obtain the final estimation for the effective constants in Table 6. Further details will be given in the subsequent papers.

Table 6
Effective rotational constants for the ground state of methylamine

Constant	Observed [a]	Calculated [b]	Difference
R_J (MHz)	22169.39	22159.96	9.43
R_k (MHz)	80986.4	81327.7	−361.3
Δ_{as} (MHz)	460.51	464.26	−4.75
ρ	0.64973 [c]	0.64976	−0.00003

[a] Values derived from Ref. [26].
[b] From B-P86/6-311G(d) data.
[c] Ref. [27].

4. Conclusion

The main findings of this paper are the following:

The B-P86/6-311G(d) method provides a good equilibrium geometry, inversion barrier and harmonic force field for the methylamine. The results show superior agreement with the corresponding experimental results than the HF, MP2 and CCD results. The inclusion of the exact HF exchange functional proposed by Becke worsens the agreement with the experimental geometry for methylamine. The above-mentioned properties of the B-P86 method make it suitable for providing functions of the structural parameters as a function of the inversion–internal rotation coordinates. We calculated four effective rotational constants from the B-P86 results and found reasonable agreement with the experimental effective values.

Acknowledgements

References

[1] T. Itoh, J. Phys Soc. Japan 11 (1956) 264.
[2] M. Tsuboi, A.Y. Hirakawa and K. Tamagake, Proc. Japan Acad. 42 (1966) 795.
[3] M. Kręglewski, J. Mol. Spectry. 72 (1978) 1.
[4] J.T. Hougen, P.E. Bunker and J.W.C. Johns, J. Mol. Spectry. 34 (1970) 136.
[5] M. Kręglewski, J. Mol. Spectry. 133 (1989) 10.
[6] L. Sztraka, Acta Chim. Hung. 124 (1987) 865.
[7] R. Krishnan, J.S. Binkley, R. Seeger and J.A. Pople, J. Chem. Phys. 72 (1980) 650; D.J. DeFrees, J.S. Binkley and A.D. McLean, J. Chem. Phys. 80 (1984) 3720.
[8] A.D. Becke, Phys. Rev. A 38 (1988) 3098.
[9] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
[10] J.P. Perdew, Phys. Rev. B 33 (1986) 8822.
[11] S.H. Vosko, L. Wilk and M. Nussair, Can. J. Phys. 58 (1980) 1200.
[12] M.J. Frisch, G.W. Trucks, M. Head-Gordon, P.M.W. Gill, M.W. Wong, J.B. Foresman, B.G. Johnson, H.B. Schlegel, M.A. Robb, E.S. Replogle, R. Gomperts, J.L. Andres, K. Raghavachari, J.S. Binkley, C. Gonzalez, R.L. Martin, D.J. Fox, D.J. DeFrees, J. Baker, J.J.P. Stewart, and J.A. Pople,

GAUSSIAN 92/DFT, Revision G (Gaussian, Inc., Pittsburgh PA, 1993).

[13] R. Krishnan, M.J. Frisch and J.A. Pople, J. Chem. Phys. 72 (1980) 4244, and references therein.

[14] J. Čížek, J. Chem. Phys. 45 (1966) 4256; J. Paldus, J. Cizek and I. Shavitt, Phys. Rev. A 5 (1972) 50; G.D. Purvis and R.J. Bartlett, Intern. J. Quantum Chem. 14 (1978) 516; J.A. Pople, R. Krishnan, H.B. Schlegel and J.S. Binkley, Intern. J. Quantum Chem. 14 (1978) 545; G.D. Purvis and R.J. Bartlett, J. Chem. Phys. 76 (1982) 1910; J.A. Pople, M. Head-Gordon and K. Raghavachari, J. Chem. Phys. 87 (1987) 5968; R.J. Bartlett, Theoret. Chim. Acta 80 (1991) 71.

[15] W.J. Hehre, J.A. Pople, P. von R. Schleyer and L. Radom, Ab initio molecular orbital theory (Wiley, New York, 1986).

[16] A. Rauk, R. Dutler and D. Yang, Can. J. Chem. 68 (1990) 258.

[17] Y. Xie, G.E. Scuseira, B.F. Yates, Y. Yamaguchi and H.F. Schaefer III, J. Am. Chem. Soc. 111 (1989) 5181.

[18] K. Takagi and T. Kojima, J. Phys. Soc. Japan 30 (1971) 1145.

[19] T. Ijima, Bull. Chem. Soc. Japan 59 (1986) 853.

[20] H.K. Higginbotham and L.S. Bartell, J. Chem. Phys. 42 (1965) 1131.

[21] C. Bergelot, V. Stern, N. Goff, J. Kachmarsky and K.D. Möller, J. Mol. Spectry. 92 (1982) 91.

[22] M. Tsuboi, A.Y. Hirakawa and K. Tamagake, J. Mol. Spectry. 22 (1967) 272.

[23] V. Spirko, J. Mol. Spectry. 101 (1983) 30.

[24] A.P. Gray and R.C. Lord, J. Chem. Phys. 26 (1957) 690.

[25] Y. Hamada, N. Tanaka, Y. Sugawara, A.Y. Hirakawa and M. Tsuboi, J. Mol. Spectry. 96 (1982) 313.

[26] N. Ohashi, K. Takagi, J.T. Hougen, W.B. Olson and W.J. Lafferty, J. Mol. Spectry. 12 (1987) 443.

[27] M. Kręglewski and G. Wlodarczak, J. Mol. Spectry. 156 (1992) 383.