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headgroup and differing only slightly in alkyl chain length[4]. When head groups are different, mixing is not ideal. It is clear that the mixing properties of lipid depend on the factors that determine packing of the chains as well as the interaction between the polar groups. Mixing in the gel phase is particularly constrained because of a close packed organization.

Biological membranes are a complex mixture of phospholipid species which very with respect to both their lipid headgroups and to their associated acyl chains. As a result they do not exhibit a single well defined lipid phase transition where all of the lipid progresses from a solid to a fluid state at a well-defined temperature.

The organizational change in a bilayer that accompant a gel-to-liquid crystalline phase change is reflected in heat capacity. Heat capacity (C_p) was calculated employing equation (7). The change of heat capacity for different mole fractions of DSPC in mixed lipids at main transition temperature was shown in Figure 5. The larger C_p was, the sharper the endothermic peak became. DPPC:DSPC (60:40 mol% and 50:50 mole%) liposomes have the lower C_p than those of the others. These mixed phospholipids in gel state contain defects responsible for the formation of large angle grain boundaries of disordered region between two lipids differing in orientation or spacial arrangement. DPPC:DSPC (50:50 mol%) liposomes, of which the transition rate is the slowest of the mixed liposomes, had pronouncely reduced cooperative unit by 0.5 mM phenothiazine derivatives (not shown at this paper). Cooperative unit is the number of molecules forced to cooperate in the transition. The sharpness of a phase transition depends upon the cooperative unit.

References

1. A. Nicolussi, S. Massari and R. Colonna. *Biochemistry*, 21, 2134 (1982).
2. M. C. Blok, L. L. M. Deenen and J. De Gier, *Biochim. Biophys.*, 433, 1 (1976).
3. K. Jacobson and D. Papahadjoloulos, *Biochemistry*, 14, 152 (1975).
4. M. K. Jain and R. C. Wagner, Introduction to biological membranes, John Wiley and Sons, Inc., 87 (1980).
5. Y. Barenholz, B. J. Litmann, T. E. Thompson and F. D. Carlson, *Biochemistry*, 16, 2806 (1977).
6. D. Papahadjopoulos, *Biochim. Biophys. Acta.*, 211, 467 (1970).
7. M. A. Singer and M. K. Jain, *Can. J. Biochem.*, 58, 815 (1980).
8. J. M. Steim, *Methods in Enzymology*, 32, 262 (1974).
9. D. Papahadjopoulos, *J. Colloid and Interface. Sci.*, 58, 459 (1977).
10. J. M. Sturtevant, *Proc. Natl. Acad. Sci.*, USA., 79, 3963 (1982).
11. S. M. Mabrey and J. M. Sturtevant, *Proc. Natl. Acad. Sci.*, USA., 73, 3862 (1976).
12. E. N. Serrallach, G. H. de Hass and G. G. Shipley. *Biochemistry*, 23, 713 (1984).
13. M. D. Houslay and K. K. Stanly, *Dynamics of biological membranes*, John Wiley and Sons, 39 (1982).
14. D. Hoekstra and O. C. Martin, *Biochemistry*, 21, 6097 (1982).
15. M. Caffrey and G. W. Feigenson, *Biochemistry*, 23, 323 (1984).

A Theoretical Investigation of FCO and FCO$^+$

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Ab initio calculations with MP3 and CISD method were performed for the FCO and FCO$^+$. The equilibrium geometry of FCO shows the reasonable agreement with experimental values. FCO$^+$ has a linear geometry with R_{CF}= 1.213 and R_{CO}= 1.118 Å. The quadratic force constants of FCO$^+$ are 23.21 md Å^{-1} for CO stretch and 12.38 md Å^{-1} for CF stretch. The cubic force constants and the other molecular constants are also calculated.

Introduction

The fluoroformyl radical. FCO has been the subject of many theoretical and experimental works. Because of its large reactivity the experimental works has been done mainly in low-temperature matrices. Milligan *et al.*[1] observed the three fundamental bands of FCO in both a CO and an Ar matrix. The three vibrational fundamentals appear at 1855, 1018, 616 cm^{-1}. Later, Jacox[2] extended the work and studied in more detail the vibrational and electronic spectra of FCO in Ar matrix. The three fundamental absorptions of FCO were found at 1857, 1023, 627.5 cm^{-1}. Adrian *et al.*[3,4] observed the ESR spectrum of FCO in a CO matrix and concluded that FCO is a σ radical with the large fluorine hyperfine splittings.

The FCO radical in the gas phase was detected by Jonathan *et al.*[5] using photoelectron spectroscopy. They observed the ionization potential of FCO and the deformation vibra-

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tional band of FCO[+] at 650 cm^{-1}. The first spectroscopic investigation on the molecular structure of FCO in the gas phase have been performed by Hirota *et al.*[6]

The infrared diode laser spectra of FCO were analyzed to determine the rotational constants, the centrifugal distortion constants and spin-rotation interaction constants. With these molecular constants the molecular structure was found to be R_{CF} = 1.334 Å, R_{CO} = 1.169 Å, $\angle$FCO = 127.3°. Lately Dornhöfer and Hack[7] have observed the laser induced fluorescence spectra of FCO and have found the collision lifetime of the emitting state to be ~40 ns.

A few quantum-mechanical calculations on FCO have been reported. Gordon and Pople[8] have calculated the equilibrium geometry using INDO method. Also Peterson[9] has calculated the spin densities with the same method. The *ab initio* SCF calculationn of FCO by McCain and Palke[10] gave rather unrealistic geometry. (R_{CO} = R_{CF} = 1.197 Å, $\angle$FCO = 134.25°) The calculation of Bleicher and Botschwina[11] gave the force constants and the geometry of FCO, R_{CF} = 1.35 Å, R_{CO} = 1.168 Å, $\angle$FCO = 128.47° which was determined by force relaxation method of Pulay.[12] Another *ab initio* SCF calculations were performed by Hinchliffe[13] to give geometry and population indices of FCO. Some low-lying electronic states of FCO have been studied by *ab initio* calculation of So.[14]

Therefore the ground state geometry of FCO has been well determined experimentally and theoretically. Compared to FCO, the moleculare ion FCO[+] has not been studied at all. Recently astrophysical work has shown that the molecular ions are widely distributed in the interstellar medium and has provided a great deal of information on their chemistry and dynamical condition. Many of the unstable molecular ions have been studied to give the properties and geometries.[15-17] For FCO[+], however, no experimental search has been tried and the only data are available from the Botschwina's calculation.[11] That shows the equilibrium geometry of FCO[+] to be linear with R_{CO} = 1.105 Å, R_{CF} = 1.233 Å.

In this paper we investigate the geometry and the properties of FCO[+] more precisely with Moller-Plesset (MP) perturbation method[18] and the configuration interaction (CI) method. The same methods of calculations are also tried on FCO to compare the results with the known values and to get some idea for the empirical corrections.

Calculation and Results

1. FCO. All calculations were performed with the GAUSSIAN 82 and 86 program. The ground state of FCO is [2]A' with an electronic configuration .... $(9a')^2(2a'')^2(10a')^1$. For the initial guess structure the optimization was carried out with unrestricted Hatree-Fock wavefunction and 3-21G basis set. The optimized geometries are R_{CF} = 1.342 Å, R_{CO} = 1.168 Å and $\angle$FCO = 128.6°. Around this geometry the single point calculations were performed with the third-order Moller-Plesset perturbation (MP3) method using 6-31G[19]* basis set. To obtain the potential energy function more than 25 single point energies were calculated in the range -0.4 Å $\leq$ R $\leq$ +0.5 Å, where the R is the optimized bond length by HF/3-21G.

The dependence of the potential on the two stretching coordinates was evaluated by fitting these single point energies

Table 1. The Coefficients of Potential Energy Function (Stretching Coordinates Only) of FCO

$C_{ij}{}^a$			
i (C-F)	*j* (C-O)	UHF/6-31G*	MP3/6-31G*
0	2	0.486579	0.598200
0	3	-0.626282	-0.629950
0	4	0.437779	0.246099
0	5	-0.394032	0.419039
0	6	0.197128	0.319108
1	1	0.111706	0.115800
1	2	0.096572	0.139638
2	1	0.503392	2.103455
2	2	2.024383	10.029430
2	0	0.183563	0.189403
3	0	-0.261831	-0.242462
4	0	0.146771	0.223150
5	0	0.149987	-0.145465
6	0	0.095163	0.027261

[a]Units are given in atomic units.

Table 2. The Coefficients of Potential Energy Function (Angle Only) of FCO

$C_i{}^a$	MP3/6-31G*	UHF/6-31G*
C_2	0.218774	0.206769
C_3	-0.055422	0.085613
C_4	-0.048449	-0.147292
C_5	0.012559	-0.146341
C_6	0.028387	-0.167090

[a]Units are given in atomic units and radians.

to the following polynomial.

$$V - V_e = \sum_{ij} C_{ij} \Delta R_1^i \Delta R_2^j \tag{1}$$

The internal coordinates ΔR_1 and ΔR_2 refer to CF stretch and CO stretch respectively. The FCO angle is fixed at 127° while the stretching coordinates are varied. The parameters of the polynomial function are given in Table 1. The unrestricted Hatree-Fock energies are also calculated and the potential function was obtained. The polynomial function is 6th order in both *i*, *j* and 2nd order in cross-terms. All the coefficients seem to be reasonable but C_{21} and C_{22} terms are very large. Probabley the number of data points which correlate two stretching coordinates were not enough, and the cross terms could not be determined very accurately.

Then we have calculated 12 more single point MP3 and UHF energies by varying the angle of FCO. The C-F and C-O bond lengths are fixed at 1.33 Å and 1.18 Å respectively while the angle is varied. The dependence of potential on the angle was studied by fitting these points to 6th order polynomial function. The coefficient of the potential function are given in Table 2. The equilibrium geometry was obtained from the both potential functions and those data are listed in Table 3 with the total energy of FCO. The geometries of this work are compared with the experimental data and the pre-

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Table 3. The Equilibrium Geometry and the Total Energy of FCO from UHF and MP3 Calculation

	UHF/6-31G*[a]	MP3 6-31G*[a]	SCF ref. 11	SCF ref. 13	exp ref. 6
R_{CF} (Å)	1.303	1.332	1.350	1.34	1.334
R_{CO} (Å)	1.155	1.164	1.168	1.16	1.169
$\angle$FCO (°)	128.53	127.85	128.47	127	127.3
V_e (a.u.)	-212.109810[b]	-212.557619[b]			

[a] Bond lengths and angles are obtained from the separate fit of potential function. [b] The V_e values are from the fit of stretching coordinates.

Table 4. The Force Constants from the Potential Fundation of FCO

	SCF ref. 11	UHF/6-31G*	MP3/6-31G*
F_{RR} (CO stretch)[a]	14.73	15.151	18.627
F_{rr} (CF stretch)[a]	5.079	5.716	5.898
F_{Rr} (CO, CF stretch-stretch)[a]	1.437	1.739	1.803
F_{RRR} (cubic CO stretch)[b]	-19.207	-18.426	-18.534
F_{rrr} (cubic CF stretch)[b]	-7.87	-7.704	-7.134
$F_{\alpha\alpha}$ ($\angle$FCO bend)[c]	1.527	1.803	1.908
$F_{\alpha\alpha\alpha}$ (cubic $\angle$FCO bend)[d]	-0.224	0.373	-0.242

[a] Units are md Å^{-1}. [b] Units are md Å^{-2}. [c] Units are md Å rad^{-2}, [d] Units are md Å rad^{-3}, Cubic force constants are defined as $F_{iii} = 1/3! \frac{\partial^3 E}{\partial \varepsilon_i^3}$

vious SCF calculation values. In their calculations Botschwina[11] used an uncontracted (7, 3) gaussian basis set and Hinchliffe[13] used Dunning's sp set (11, 6) Contracted to (5, 4).

The force constants were calculated from the coefficients of potential function and compared with the values of Botschwina et al.[11] in table 4. Most of the force constants agree well with previous calculated values, but the quadratic force constant of CO stretch from MP3 calculation is high, which is much higher than the experimental value,[20] 14.3 md Å^{-1}. The fit of two stretching coordinates of FCO was very sensitive with energy points. Not enough data points might cause a small deviation in the potential function and this could influence the force constants.

After MP3 calculation we tried CI calculation on FCO using 6-31G* and 6-311G*[21] basis set. The orbitals used in CISD calculation are 45 α-orbitals (12 occupied, 33 virtual) and 45 β-orbitals (11 occupied and 34 virtual) obtained from SCF calculation. Since the CI method takes long computation time, the calculations were carried out at the point near the equilibrium geometry obtained in MP3 calculation. In the calculation the $\angle$FCO is fixed at 127.0 while the C-F and C-O distances are varied. The results of calculation are given in Table 5. This CI energies are corrected by size-consistency factor. From the minimum energy point the optimum geometry can be estimated. For the CISD/6-31G* calculations the minimum energy is reached at R_{CF} = 1.34 Å, R_{CO} = 1.18 Å. On the other hand the CISD/6-311G* calculations indicate the minimum energy at R = 1.33 Å, R_{CO} = 1.17

Table 5. The Total Energies of FCO by CISD Calculation

R_{CF} (Å)	R_{CO} (Å)	CISD/6-31G* (a.u.)	CISD/6-311G* (a.u.)
1.30	1.18		-212.681992
1.31	1.18	-212.571890	-212.682296
1.32	1.18	-212.572274	-212.682456
1.33	1.16	-212.571707	
1.33	1.17	-212.572305	-212.682747
1.33	1.18	-212.572510	-212.682481
1.33	1.19		-212.681870
1.34	1.18	-212.572611	-212.682384
1.35	1.18		-212.682172
1.38	1.18	-212.571840	
1.43	1.18	-212.568864	

Table 6. The Rotational Constants and Dipole Moments of FCO.

	A	B	C	μ
		(MHz)		(D)
MP3/6-31G*	191359.9	11475.95	10826.67	1.243
CISD/6-31G*	181915.2	11346.20	10680.07	1.338
CISD/6-311G*	184875.0	11527.62	10851.02	1.219
SCF (ref. 11)	192636	11209	10593	1.08
SCF (ref. 14)				1.33
exp. (ref. 11)	191200	11466.15	10795.23	

Å, which is more closest to the experimental value, the geometry optimization is more desirable for the better structure, if the number of data points are enough to get potential energy function.

The other molecular constants, rotational constants and dipole moments of optimized structure, were calculated and are listed in Table 6 with the reference values.

2. FCO⁺. The ground state of FCO⁺ is $^1\Sigma^+$ with an electronic configuration .... $(6\sigma)^2 (1\pi)^4 (7\sigma)^2 (2\pi)^4$. This singlet state of FCO⁺ makes the calculation much easier than FCO molecule. The first optimization for the geometry of FCO⁺ was performed with HF/3-21G level. The geometry was converged at R_{CF} = 1.228 Å, R_{CO} = 1.103Å and $\angle$FCO = 180.8°. Therefore the FCO⁺ is linear molecule as predicted by Botschwina.[11] The linearity was confirmed by checking with higher level of calculation. And throughout all calculations the $\angle$FCO was fixed at 180°. From the results of calculation it can be realized that the bond lengths are shortened considerably by ionization of the molecule.

For the potential energy function of FCO⁺ the single point energy was calculated with MP3/6-31* method. More than 30 points of energies were obtained in the range -0.3 Å $\leq R \leq$ +0.3 Å, where R is the optimized bond length by HF/3-21G. The potential dependence on the two stretching coordinates was evaluated by fitting the previous polynomial function (1) to those energy points.

The results of fitting are given in Table 7. The coefficients of the potential function are increased in both C-F and C-O stretching internal coordinates. Since the bond lengths decrease considerably upon ionization, it seems reasonable. The force constants calculated from those coefficients of potential function are listed in Table 8 with the Botschwina's

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Table 7. The Coefficients of the Potential Energy Function of FCO$^+$ (Stretching Coordinates Only)

i (C–F)	$C_{ij}{}^a$ j (C–O)	MP3/6–31G*
0	2	0.745218
0	3	-0.886874
0	4	0.707553
0	5	-0.503099
0	6	0.110542
1	1	0.050176
1	2	0.003869
2	1	-0.049319
2	2	0.015570
2	0	0.397710
3	0	-0.502339
4	0	0.387397
5	0	-0.269420
6	0	0.159832

^{a} Units are given in atomic units

Table 8. The Force Constants from the Potential Function of FCO$^+$

	MP3/6–31G*	SCF ref. 11
F_{RR} (CO stretch)^a	23.206	23.36
F_{rr} (CF stretch)^a	12.384	10.96
F_{Rr} (CO, CF stretch-stretch)^a	0.781	0.579
F_{RRR} (cubic CO stretch)^b	-26.093	
F_{rrr} (cubic CF stretch)^b	-14.780	

^{a} Units are md Å^{-1}. ^{b} Units are md Å^{-2}

Table 9. The Equilibrium Geometry and the Total Energy of FCO$^+$

	MP3/6–31G*	SCF ref. 11
R_{CF} (Å)	1.213	1.233
R_{CO} (Å)	1.118	1.105
∠FCO (°)	180.0	180.0
V_e (a.u.)	-212.226757	-211.44045

values. The quadratic force constant of C–O stretch of HCO$^+$ is 24.74 md Å^{-1}, which also agrees with out value. The equilibrium geometry obtained from fitting is shown in Table 9. The C–F bond length is shorter and the C–O bond length is longer than the values of Botschwina. The R_{CO} of HCO^{+22} is 1.101 Å, which is also shorter than our value.

For more accurate data of equilibrium geometry and other properties, the CISD/6–31G* and CISD/6-311G* calculations were performed. Also MP3 calculation with the larger basis set have been tried. In this basis set Huzinaga's (10s, 6p, 2d) primitive basis functions[23] are contracted to (5s, 3p, 2d) by Dunning's contraction scheme.[24] The exponent of d polariza-

Table 10. The Energies Calculated with CISD/6–31G*, CISD/6-311G* and MP3/Dunning's

R_{CF} (Å)	R_{CO} (Å)	CISD/6–31G*	CISD/6-311G* (a.u.)	MP3/Dunning's
1.18	1.12		-212.354637	
1.19	1.11		-212.355052	
1.19	1.12		-212.355130	-212.389472
1.20	1.10		-212.354674	-212.389929
1.20	1.11		-212.355256	-212.390067
1.20	1.12	-212.241794	-212.355319	-212.389679
1.20	1.13		-212.354900	-212.388800
1.21	1.11	-212.241500		
1.21	1.12	-212.242182	-212.355228	-212.389606
1.21	1.13	-212.242352		
1.21	1.14	-212.242045		
1.22	1.12	-212.242287	-212.354875	-212.389272
1.23	1.12			-212.388696

Table 11. The Rotational Constants, Vibrational Frequencies and Dipole Moments of FCO$^+$

	MP2/6–31G*	MP3/6–31G*	CISD/6–31G*	CISD/6-311G*
B (MHz)	10429.2	10662.3	10589.3	10772.4
μ (D)	0.7111	0.5645	0.7059	0.6367
ω_1 (cm^{-1})	2546			
ω_2 (cm^{-1})	1191			
ω_3 (cm^{-1})	545			
ω_4 (cm^{-1})	545			

tion functions are chosen 1.5, 0.5 for F, 1.0, 0.5 for C[25] and 1.5, 0.5 for O[26,27]. All these single point energies are listed in Table 10. From these values the optimum geometry can be estimated at the minimum energy point. In the CISD/6–31G* calculations R_{CF}= 1.21 Å, R_{CO} = 1.13 Å and in the CISD/6-311G* calculations R_{CF}= 1.20 Å, R_{CO}= 1.12 Å. The MP3/Dunning's calculation show shortest bond lengths of R_{CF}= 1.20, R_{CO} = 1.11 Å. Since there is no experimental data to compare, it is hard to predict which values are the optimum geometry for FCO$^+$.

It is interesting to note that the calculation with the larger basis set gives shorter bond length in MP3 calculation.

In the case of FCO$^+$ the ground electronic state is singlet, and it was possible to carry out the optimization with MP3/6-31G*. The optimized structure was R_{CF}= 1.213 Å, R_{CO}= 1.118 Å, which agree very well with our value from the potential function. The quadratic force constants calculated from the optimization were F_{RR}= 23.493 md Å^{-1}, F_{rr}= 12.101 md Å^{-1}, which also give good agreement with our value. The total atomic charge of FCO$^+$ are appeared to be - 0.01 on F, + 1.12 on C and - 0.11 on O.

The calculation of vibrational frequencies have been tried with MP2/6–31G*. These fundamental frequencies are listed in Table 11 along with dipole moments and the rotational constants. The values shown in Table 11 were calculated with the optimized geometry for MP2 and MP3, and with the geometry of minimum energy for CISD.

Discussion

As mentioned previously, in the case of FCO fitting with the potential function to the energy points is very sensitive to the energy. The energy points are in the range of -0.4 Å $\leq R \leq +0.5$ Å. If we narrow down to the range of -0.2 Å $\leq R \leq +0.2$ Å, the fit gives closer value of force constants and the equilibrium geometry to the experimental value. But the fit is not converged to the stationary point and the higher order coefficients of potential function are diverged. This situation might be improved with enough data points around the equilibrium geometry. Particulary the quadratic force constant of MP3 is too high, compared to the experimental value,[20] 14.3 md A^{-1}. As we noticed in the previous paper,[28] the MP3 calculations give the steeper curve in the potential function than the CI calculations. Even the MP3 method gives lower energy in single point clacnlation the shape of whole potential function is very different from that of CI method This effect may be one of the serious reasons that give the big force constant. In this point of view, the potential function of CI calculation will improve the situation.

Compared to FCO, the FCO$^+$ is much more favorable molecule in the calculation. Since its simplicity of calculation, it is possible to carry out the calculation with the advanced method and bigger basis set. Therefore the data obtained for FCO$^+$ are believed to be reliable for the experimental search. The vibrational frequencies were not obtained with the upper level of method and those values could be improved further. The quadratic and cubic force constants of FCO$^+$ are much larger than those of FCO, and this fact can be expected from the shorter bond lengths of FCO$^+$. The C–O bond length is little longer than the value of Botschwina[11] and also longer than the value of HCO.$^+$[22] Considering the value from the CI method, the longer value of R_{CO} seems favorable. Further calculations for the other molecular parameters are possible for FCO$^+$, which may be helpful for the search of the molecule.

References

1. D. E. Milligan, M. E. Jacox, A. M. Bass, J. J. Comeford and D. E. Mann, *J. Chem. Phys.*, **42**, 3187 (1965).
2. M. E. Jacox, *J. Mol. Spectrosc.*, **80**, 257 (1980).
3. F. J. Adrian, E. L. Cochran and V. A. Bowers, *J. Chem. Phys.*, **43**, 462 (1965).
4. E. L. Cochran, F. J. Adrian and V. A. Bowers, *J. Chem. Phys.*, **44**, 4626 (1966).
5. J. M. Dyke, N. Jonathan, A. Morris and M. J. Winter, *J. Chem. Soc., Faraday Trans. 2*, **77**, 667 (1981).
6. K. Nagai, C. Yamada, Y. Endo and E. Hirota, *J. Mol. Spectrosc.*, **90**, 249 (1981).
7. G. Dornhöfer and W. Hack, Report MPIS, *Sci. Tech. Aerosp. Rep.*, **24**(21), (1986).
8. M. S. Gordon and J. A. Pople, *J. Chem. Phys.*, **49**, 4643 (1968).
9. L. Pedersen, *J. Mol. Struct*, **5**, 21 (1970).
10. D. C. McCain and W. E. Palke, *J. Chem. Phys.*, **56**, 4957 (1972).
11. W. Bleicher and P. Botschwina, *Mol. Phys.*, **30**, 1029 (1975).
12. P. Pulay, *Mol. Phys.*, **17**, 197 (1969).
13. Hinchliffe, *J. Mol. Struct.*, **64**, 117 (1980).
14. S. P. So, *J. Mol. Struc.*, **110**, 167 (1984).
15. S. C. Foster and A. R. W. Mckellar, *J. Chem. Phys.*, **81**, 3424 (1984).
16. E. Schäfer, R. J. Saykally, and A. G. Robiette, *J. Chem. Phys.*, **80**, 3969 (1984).
17. C. S. Gudeman and R. C. Woods, *Phys. Rev. Lett.*, **48**, 1344 (1982).
18. W. J. Hehre, L. Radom, P. V. R. Schleyer and J. A. Pople, "*Ab initio* Molecular Orbital Theory", John Wiley & Sons, Inc. New York, 1986
19. M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. Defrees, and J. A. Pople, *J. Chem. Phys.*, **77**, 3654 (1982).
20. J. S. Shirk and G. C. Pimentel, *J. Am. Chem. Soc.*, **90**, 3349 (1968).
21. R. Krishnan, M. J. Frisch and J. A. Pople, *J. Chem. Phys.*, **72**, 4244 (1980).
22. P. Botschwina, *Chem. Phys. Letter*, **29**, 28 (1974).
23. S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1970).
24. T. H. Dunning Jr., *J. Chem. Phys.*, **55**, 716 (1971).
25. S. Rothenberg and H. F. Schaefer III, *J. Chem. Phys.*, **54**, 2764 (1971)
26. P. Botschwina and P. Rosmus, *J. Chem. Phys.*, **82**, 1420 (1985).
27. B. Roos and P. Siegbahn, *Theoret. Chim. Acta*, **17**, 199 (1970).
28. E. M. Sung, *Bull. Korean Chem. Soc.*, **10**(4), 377 (1989).