

## Ab Initio MO Study of Hydrogen Bonding in Methyl Fluoride Cyclic Trimer

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**Summary:** Ab initio SCF-MO calculations of the interaction energies; changes in electronic charges distributions and dipole moments using the 4-31G and 6-31G basis sets are given for methyl fluoride dimer and cyclic trimer. A considerable deviation from additivity in hydrogen bond energies has been found. The importance of this non-pair additivity has been discussed.

### Introduction

Methyl fluoride (MeF) is one of the suitable models of polyatomic molecules for studying the absorption of laser radiations and its subsequent energy transfer through specific energy flow paths [1,2]. The dependence of laser output power as a function of MeF pressure has been also investigated [3,4]. A study of the different molecular interactions such as hydrogen bonding might help in the description of certain properties of MeF in its gaseous or condensed phases.

On the other hand it has been found [5] that non-pair additivity of interaction energies in multimer structures is an important factor to take into consideration when structuring a molecular dynamics algorithm for polar liquids. This non-additivity has been clearly found for water by ab initio calculations [6,7].

If non-pair additivity is significant in a polar liquid such as MeF, then an algorithm which avoids the assumption of pairwise energy interaction should be used for molecular dynamics simulations. It is the purpose of this paper to investigate these points and

to report the results of ab initio SCF-MO calculations of the hydrogen bond dissociation energies dipole moments and changes in electronic charge distributions on dimer or cyclic trimer formation in MeF. It is also to study the effect of basis sets on the calculated properties reported here.

### Method of Calculations

The hydrogen bond was assumed linear as shown below.

The angle  $\theta$  was fixed at  $49^\circ$  which from geometrical considerations leads to a perfect cyclic trimer. Variations of R have been considered. The monomer geometry was kept at its experimental values [8] with the C-H and C-F distances taken to be  $1.106 \text{ \AA}$  and  $1.385 \text{ \AA}$  respectively and the  $\angle \text{F-C-H}$  bond angle set equal to  $109.033^\circ$ . The intermolecular geometries are retained during the intermolecular interactions. In order to assess the strength of the dimer interaction in the cyclic trimer, the pair of MeF molecules have been assumed the same relative positions of two adjacent molecules in the cyclic trimer.

The calculations were carried out on the Honeywell-6080/CDC-7600 system of Aberystwyth/UMRCO using the Gaussian 76 program of Pople and Co-Workers [9]. The well characterized split valence basis sets: 4 - 31G

Experimental study of hydrogen bonding in MeF dimer predicted a hydrogen bond strength of 6.284 KJ/mol [20]. Thus, the calculated hydrogen bond strength using the 6 - 31G basis set level show a more reasonable agreement with the experimental value than the 4 - 31G basis value. However, the different calculated properties for MeF dimer at its equilibrium geometry studied here are in a correct correlation with different systems studied before. With MeF molecule as a common proton acceptor the interaction energy with HF, HOH and HNH<sub>2</sub> as proton donors were calculated

to be 34.812; 23.585 and 14.495 KJ/mol respectively and the equilibrium distances R were found to be 2.71, 2.92 and 3.24 Å respectively [15,21]. The results obtained here, Table 2, are in the correct order predicting that MeF molecule is the weakest proton donor among the above mentioned molecules and having the longest intermolecular separation as expected. It has to be noted here that the lower dimerization energy and the different electronic charge distribution obtained by using the 6 - 31G basis set are largely due to a better description of the core orbitals on the carbon and fluorine atoms and which may not significantly affect the calculated dipole moment.

#### *b) Cyclic trimer of MeF*

It has been shown in the preceding section that the calculated atomic charges derived from the population analysis either using the 4 - 31G or

the 6 - 31G basis sets indicated a tendency for the formation of additional hydrogen bonds. It has been sought here to determine quantitatively the additivity or non-additivity of hydrogen bond energies by studying a cyclic trimer as the simplest cyclic polyerms of MeF and which is expected to be a quite stable structure, since an additional hydrogen bond is formed. It is also aimed here to investigate whether mutual polarizations of bonded molecules in such cyclic polymeric structure will lead to an enhancement of hydrogen bond energies which may overcome the stability loss due to ring strain. It is required that the newly added MeF molecule to the dimer leading to the cyclic trimer is positioned in such a way that it forms with each one the same equilibrium form of the dimer studied above.

The total energy of this cyclic trimer arrangement was calculated to be -416.582520 a.u. and -416.988252 a.u. using the 4- 31G and 6 - 31G basis sets respectively. The trimer dipole moment was also calculated to be 0.0028 and 0.0029 D respectively. The calculated total energies show that the cyclic trimer is more stable than three separated monomers by 0.012958 a.u. (34.063 KJ) using the 4 - 31G basis set and 0.011524 a.u. (30.293 KJ) using the 6 - 31G basis set. This indicates that the strength of only one hydrogen bond is amounting to 11.354 KJ/mol and 10.098 KJ/mol using the 4 - 31G and 6 - 31G levels respectively. This difference may be attributed to the better description of the core orbitals on the carbon and fluorine atoms in case of the 6 - 31G baasis set. However, both levels have shown that mutal polarizations of hydrogen bonded molecules in this cyclic structure leads to an enhancement of hydrogen

bond energies as has been found before [6,22]. An explanation for the high stability of this cyclic trimer may be due to the increased negative charges on the fluorine atoms and the positive charges on the protons as clear from the gross atomic populations of the trimer given in Figs. 2 and 3.

It has to be noted that there is a clear non-additivity of hydrogen bond energies and any attempt to treat systems of this type in terms of pairwise interaction will be inadequate. and 6 - 31G [10-13] have been used. These basis sets have been chosen

because various properties such as hydrogen bond energies; electron density distributions and dipole moments of the interactions between MeF and HF, H<sub>2</sub>O and NH<sub>3</sub> as proton donors have been satisfactorily predicted [14-17].

## Results and Discussion

### a) Equilibrium form of the dimer

Table 1 contains the total energy of MeF dimer calculated as a function of the intermolecular distance and these results are plotted in Fig.1.

Table-1: Intermolecular potential  
for MeF dimer<sup>(a)</sup>

R(Å)	E(a.u.)	
	4-31G <sup>(b)</sup>	6-31G <sup>(c)</sup>
2.4	-277.668686	-277.938638
2.8	-277.708370	-277.978981
3.2	-277.716241	-277.987095
3.6	-277.716954	-277.988023
4.0	-277.715981	-277.987282
4.4	-277.714923	-277.986347
4.8	-277.714281	-277.985728
5.2	-277.713950	-277.985394

(a)  $\theta$  is fixed at 49°

(b) the 4-31G calculated monomer total energy is  $E = 138.856521$  a.u. and the dipole moment  $\mu = 2.5$  D.

(c) the 6-31G calculated monomer total energy is  $E = 138.992243$  a.u. and the dipole moment  $\mu = 2.5$  D.

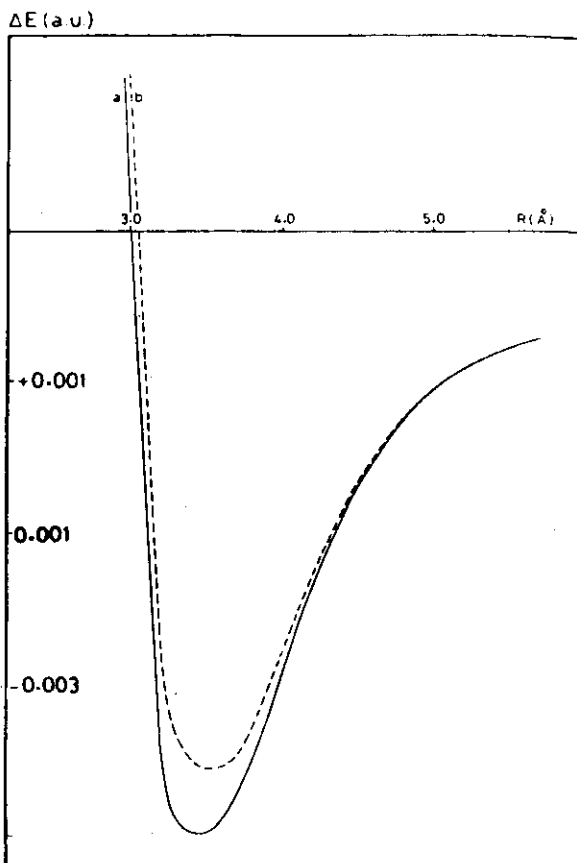


Fig.1: Interaction energy of MeF dimer as a function of intermolecular distance R.

a) using 4-31 basis set b) using 6-31 basis set.

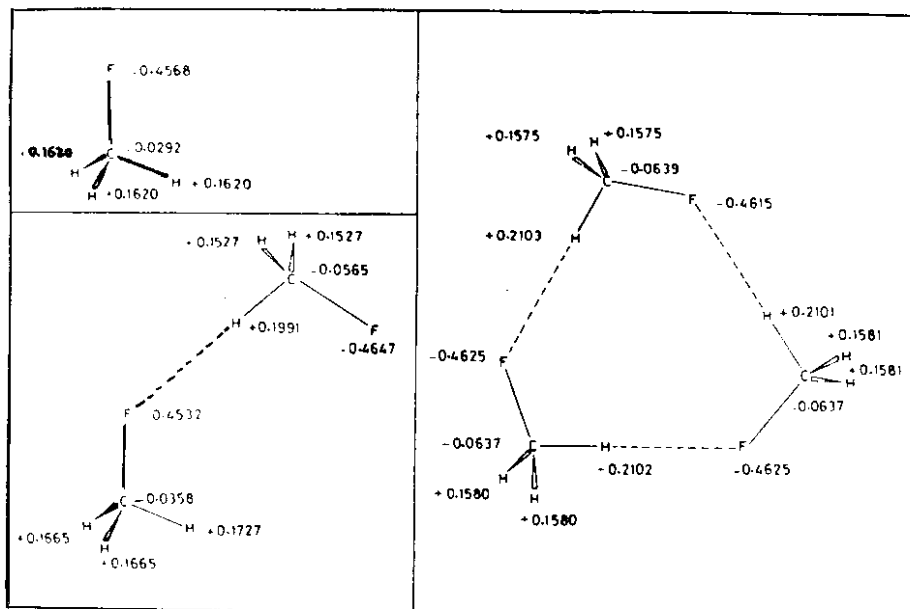


Fig. 2: Calculated gross atomic populations for the monomer, dimer and Trimer (4-31G)

Using the 4 - 31G basis set inter-molecular interaction energy has shown a minimum at an intermolecular distance  $R = 3.48 \text{ \AA}$  (Fig. 1a). The dimerization energy was found to be 0.00398 a.u. (10.463 KJ/mol) with a calculated dimer dipole moment amounting to  $\mu = 2.86 \text{ D}$ . The electronic charge distribution described by the gross atomic populations for the dimer at its equilibrium geometry is given in Fig. 2. Compared with the values for the isolated molecule, it is clear that the fluorine atom of the proton donor MeF molecule becomes more negative. Thus, this molecule will tend to become a proton acceptor for further hydrogen bonding. It may also be noted that all the hydrogen atoms of the methyl group of the proton acceptor MeF molecule become more positive and therefore its tendency to become a proton donor in further hydrogen bonding will increase. On the other hand the hydrogen atoms of the methyl group of the proton donor molecule show different trend. The proton involved

in the hydrogen bonding becomes more positive while the other two become less positive. This indicates as to be expected that no more than one hydrogen atom of the methyl group can be involved in hydrogen bond formation. The gross atomic populations on MeF molecules in the

Table-2: Calculated hydrogen bond strength<sup>(a)</sup>

	4-31G <sup>(b)</sup>	6-31G <sup>(c)</sup>	Exptl. <sup>(d)</sup>
Dimer	10.462	9.332	6.284
Trimer <sup>(e)</sup>	11.354	10.098	

(a) in KJ/mol.

(b)  $R = 3.48 \text{ \AA}$

(c)  $R = 3.55 \text{ \AA}$

(d) ref [20].

(e) the value cited is per bond.

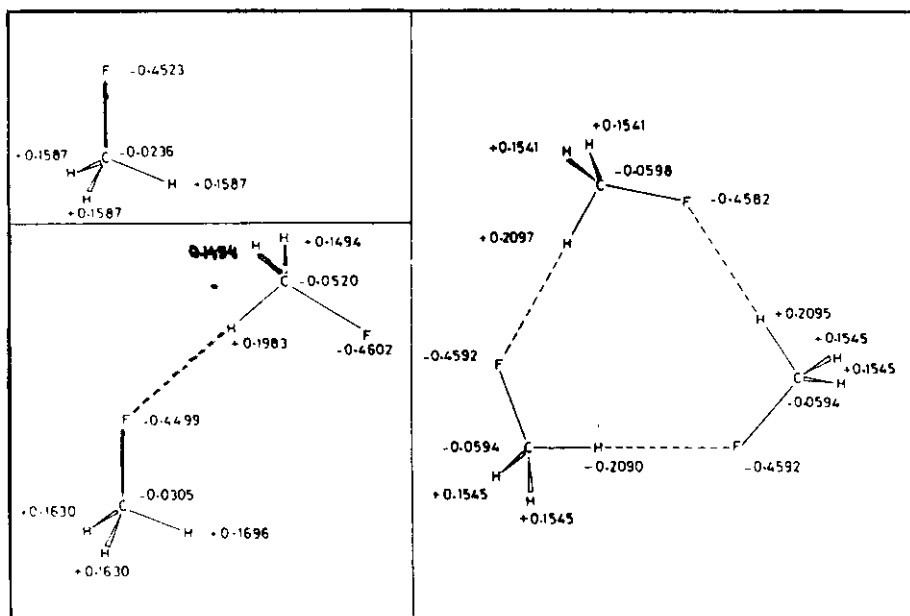


Fig.3: Calculated gross atomic populations for the monomer, dimer and Trimer (6-31G).

equilibrium dimer show that there is a charge transfer from the proton acceptor molecule to the donor one amounting to  $\sim 0.017$  electrons.

Using the 6 - 31G basis set; the intermolecular interaction energy show a minimum at an intermolecular distance  $R = 3.55 \text{ \AA}$ . The dimerization energy was found to be 0.00355 a.u. (9.332 KJ/mol) with the dimer dipole moment calculated to be 2.85 D. The calculated gross atomic populations for the dimer when compared with the values calculated for the isolated molecule show (Fig. 3) the same trends discussed above using the 4 - 31G basis set. The amount of charge transfer from the proton acceptor molecule to the proton donor molecule on dimer formation was found to be  $\sim 0.015$  electrons.

The positive charges of the hydrogen atoms and the negative charges of the carbon and fluorine atoms for the isolated molecule or for the dimer either on the proton donor or the

proton acceptor molecules are over-estimated using the 4 - 31G basis set compared to those obtained using the 6 - 31G basis set. Mutual molecular polarizations on hydrogen bond formation being slightly different, seem, however, to be predicted more reasonably using the 6 - 31G basis set. This is also clear from the relative values of calculated dimer dipole moment and the amount of charge transfer being lower than in the case of 4 - 31G basis set. It is well known that the accuracy of the calculated electron density distributions depends on the quality of the basis set used in the calculations [18,19]. Correlation effects which are neglected in single determinant SCF calculations have been also assumed not have an important effect on the calculated distributions [17-19].

The trimer interaction energy can be written as a sum of three dimeric terms plus a 3-body interaction term which becomes zero at the dimeric dissociation limits [23] as follows:

$$\Delta E_{ABC} = \Delta E_{AB} + \Delta E_{BC} + \Delta E_{CA} + \Delta E_{ABC}$$

The first three terms of the right hand side are all equivalent and each equals the dimer interaction energy and the last term  $\Delta E_{ABC}$  is the non-pair additivity. This latter term is calculated to be 2.677 KJ and 2.297 KJ using 4 - 31G and 6 - 31G basis sets respectively. While this non-pair additivity term seems to be small, it is significant at about 25% of the dimer interaction energy and at about 10% of the trimer interaction energy. As the size of the multimer increases, it is expected that this non-pair additivity term will increase in a non-linear fashion [24]. In consequence, it can be concluded that the non-pair additivity is sufficiently significant in MeF and an algorithm which avoids the assumption of pairwise energy interaction should be used for molecular dynamics simulations.

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