The fuzzy D2h-symmetries of ethylene tetra-halide molecules and their molecular orbitals

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Based on our study in relation to the fuzzy symmetry characterization and the application to linear molecule, the fuzzy symmetry of the planar molecules have been analyzed. The prototypical planer molecules we have chosen to study are the C_2F_3X ($X = Cl$, Br, and I) and three kinds of $C_2F_2Cl_2$ isomers. These molecules relate to the fuzzy symmetry in connection with the D2h point group. As we known, the D2h point group includes an identity transformation and seven twofold symmetry transformations but without higher-fold ones. Meanwhile, it is related only to some one-dimensional irreducible representations, but there is not to multi-dimensional irreducible representation. In this paper, the fuzzy symmetries of these molecules and their molecular orbital(MO)s have been studied, such as the membership functions, the representation compositions, the fuzzy correlation diagrams and so on have been analyzed. These analysis methods can be used to analyze the molecular fuzzy symmetries of some other molecule systems, no difficulty.

KEY WORDS: fuzzy symmetry, ethylene tetra-halide, fuzzy representation

1. Introduction

Someone asked "Are the concepts of chemistry all fuzzy?"[1]. However in theoretical chemistry region the study on the fuzzy symmetry is less. Mezey and Maruani [2,3] have researched this topic earlier, they have discussed the fuzzy symmetry caused by displacement of some atoms in some specific molecules with the symmetry of common point groups. By means of the fuzzy subgroups, Chauvin [4,5] analyzed some isomer molecular skeletal symmetry. In our previous works [6–8], the fuzzy symmetry characterizations of the molecules and linear molecular orbitals are analyzed. Now we start to study the non-linear molecule, in detail. In this paper, we will analyze the molecular fuzzy symmetries of some

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ethylene tetra-halide molecules. As for the tetra-halide molecules, they are provided with the symmetry of D2h group if all four halide atoms are same, or the fuzzy symmetry of D2h if some of the halide atoms are different.

Besides the identity transformation, the D2h group only includes some twofold symmetry transformations. It is the most complex primary point group. However, there are some twofold symmetry transformations with various membership functions included. It is different from the *Ci* point group, in which included only one twofold symmetry transformation and the identity one. Especially, for D2h point group, some different irreducible representations are included. When we analyze the fuzzy representation of molecular orbit (MO), not only the overlap between the symmetrical and asymmetrical composition, but also the overlap touching to some more kinds of various irreducible representation compositions should be considered. Therefore, for the ethylene tetrahalide, the analysis of molecular fuzzy symmetry ought to be much complex than that of simple linear molecules.

2.   Computational details

In this paper, the MO theoretical computation base often at the AM1 level. Of course, we can compute at other levels. In our previous papers [7,8], based on the AM1, STO-3G, 6-31G, and some other levels, the molecular fuzzy symmetry of some linear molecules had been analyzed, the results are similar. Based on a certain MO theorem, we can get the corresponding LCAO coefficients and analyze the molecular fuzzy symmetry. As for various MO theorem, the complicacy for the treatment method of the molecular fuzzy symmetry ought to be some differ in degree. However, the elementary principles are the same. Therefore as we get the method to analyze the molecular fuzzy symmetry at a certain MO theory, and then we may establish the method at another MO theorem, in principle.

As respects the symmetry, there is an important Noether's theorem [9, 10]. According to this theorem, there are two important concepts: the symmetry and invariable. They are relative but different concepts. The symmetry is connected with the molecular point group, but the invariable is connected with the representation (i.e. the symmetrical or asymmetrical) or generalized parity of MO [11]. The symmetry denotes the invariance of the molecule or MO under a certain transformation. But the invariable denotes the invariance of generalized parity or irreducible representation for MO. However, they are confused [11,12] in W-H theorem [13,14]. Corresponding to these two concepts, there are two important amounts for the topic of molecular fuzzy symmetry [7,8]: one is the membership function, which measures the perfection degree of the molecular symmetry; the other is the symmetrical and asymmetrical compositions, or in general speaking, the irreducible representation compositions, which measures the perfection degree of the generalized parity or representation of the

MOs. Now we turn to analyze how to calculate the membership functions and irreducible representation compositions for ethylene tetra-halides.

2.1. The membership function

Based on a certain MO theorem, we can get the membership function (designated as μ) for the symmetry transformation $\hat{G}$ of a certain point group [6,7]:

$$\mu_Y(\hat{G}/\mathbf{G}; M) = [\Sigma_J(Y_J \wedge Y_{GJ})]/[\Sigma_J(Y_J)], \tag{1}$$

where the Y_J and Y_{GJ} are the criteria of J atom and GJ atom, in which GJ is related to J atom through the symmetry transformation $\hat{G}$, respectively. As for the molecule skeleton, Y may be the atomic number or the electronic charges based on a certain MO theorem.

In respect of the membership function of MO, if there is only one AO in every one atom to form the MO, equation (1) will be true still. However if there are more than one AOs in one atom to form the MO, the equation (1) will be modified a few, and according to LCAO-MO theory, the ρth MO Ψ_ρ can be written as:

$$\Psi_\rho = \Sigma_J \, \Sigma_i a_\rho \, (J, i) \, \phi(J, i) \tag{2}$$

where $\phi(J, i)$ is the ith AO of the Jth atom, and $a_\rho(J, i)$ is the corresponding linear combination coefficient of it. The criterion of $\phi(J, i)$ may be $Y_{Ji} = a_\rho^*(J, i)a_\rho(J, i)$. If the $a_\rho(J, i)$ is real, the $Y_{Ji} = a_\rho^2(J, i)$. Therefore we get:

$$\mu_Y(\hat{G}/\mathbf{G}; M) = [\Sigma_J\Sigma_i(Y_{Ji} \wedge Y_{GJi})]/[\Sigma_J\Sigma_{Ji}(Y_{Ji})]. \tag{3}$$

If there is only one AO in every atom to combine the MO Ψ_ρ, this equation ought to be reduced to equation (1). It should be noted that there are some various symmetry transformations $\hat{G}$ in the D2h point group to which ethylene tetra-halide molecule belongs. And corresponding to various symmetry transformations, the membership functions of them are different.

2.2. The irreducible representation composition

When we analyze the fuzzy point group $(\underset{\sim}{C}i)$ of the linear molecular MO, the concepts, symmetry-composition, and asymmetry-composition are introduced. Where the so-called symmetry-composition and asymmetry-one denote the irreducible representations are symmetrical and asymmetrical one in relation to Ci point group, respectively. In this paper, the fuzzy symmetries should be connected with the D2h point group. And correspondingly, more various irreducible representations should be taken into consideration, only the symmetrical

or asymmetrical representation would be not enough. According to equation (2), for the MO-Ψ_ρ the corresponding linear combination coefficient of the ith AO of the Jth atom, $a_\rho(J, i)$, will be decomposed to denoted as the summation of some other linear combination coefficients each of which only relates to one single irreducible representation, respectively, i.e.

$$a_\rho(J, i) = a_\rho(J, i; \Gamma_1) + a_\rho(J, i; \Gamma_2) + a_\rho(J, i; \Gamma_3) + \cdots + a_\rho(J, i; \Gamma_r), \quad (4)$$

where the $\Gamma_1, \Gamma_2, \ldots, \Gamma_r$ are the various irreducible representations in regard to $a_\rho(J, i)$.

The ethylene tetra-halide molecules, we may analyze their fuzzy symmetry in related to the D2h point group. There are two carbon atoms and four halide atoms. These six atoms and corresponding serial number are shown in figure 1, together with the space axes.

If all of the four halide atoms in such a molecule are the same, such molecule ought to be provided with the D2h point group symmetry, otherwise with certain subgroup symmetry. Certainly, the symmetry of mirror with the molecular plane ought to be always existed. As for other symmetries, some of them may be existed and other may be omitted. There are four AOs for each atomic outmost shell, and they will combined to form 24 MOs. Taking C_2F_4 as the example, using methods at AM1 level within Gaussian 98 program [15], we can get the orbital irreducible representations of these 24 MOs as follows:

Occupied (Ag) (B1u) (B2u) (B3g) (Ag) (B1u) (Ag) (B2u) (B3u)
          (B3g) (B2g) (B1u) (B1g) (Au) (B3g) (B2u) (Ag)(B3u)
Virtual   (B2g) (B1u) (B2u) (Ag) (B1u) (B3g)

The occupied MOs are MO-1 to MO-18 and virtual MOs are MO-19 to MO-24, respectively.

Because the C_2F_4 molecule possesses the common D2h point group symmetry, the representations of the MO above-mentioned are "pure", i.e. such representation composition ought to be 1 and other will be 0. For six π-MOs
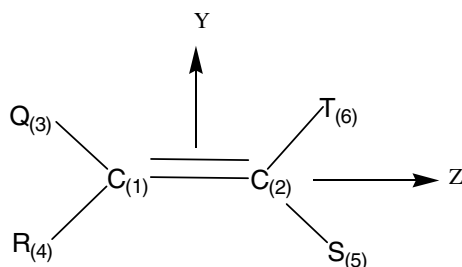

Figure 1. The space axes and atomic serial numbers (in bracket) of ethylene tetra-halide molecule. X-axis is vertical to the molecule plane and cross the CC bond. The Q, R, S, and T denote four halogen atoms (where these atoms may be different or the same).

composed from six *Px*-AOs of six atoms, the representations are 1[B1g], 2[B2g], 1[Au], 2[B3u], and for 18 σ MO from *S,Py,Pz*-AOs of six atoms, the representations are 5[Ag], 4[B3g], 5[B1u], 4[B2u]. As concerns some other ethylene tetra-halide molecules, there are six π-MOs composed from six *Px*-AOs and 18 σ-MOs from *S,Py,Pz*-AOs of six atoms, too. However, these irreducible representations are not "pure", but the overlap of some representations. The [B1g], [B2g], [Au], and [B3u] representations may overlap to compose the six π-MOs by six *Px*-AOs, and we can get the LCAO coefficients in relation with such four irreducible representations. Similarly, we may get the LCAO coefficients in relation with these four irreducible representations, [Ag], [B3g], [B1u], and [B2u] representations, in related to the 18 σ-MOs, *S,Py,Pz*-AOs. Further, we can obtain the corresponding representation-compositions for various MOs.

Now, we analyze the method to calculate the LC-*Px*-AOs coefficients of the π-MOs. For the four irreducible representations in relation to π-MOs, all of the LC-*S,Py,Pz*-AO coefficients are null, but for the LC-*Px*-AO coefficients, we can get:

$$a(1x; \text{Au}) = a(2x; \text{Au}) = 0, \tag{5.1}$$

$$a(3x; \text{Au}) = a(5x; \text{Au}) = -a(4x; \text{Au}) = -a(6x; \text{Au}), \tag{5.2}$$

$$a(1x; \text{B1g}) = a(2x; \text{B1g}) = 0, \tag{5.3}$$

$$a(3x; \text{B1g}) = a(6x; \text{B1g}) = -a(4x; \text{B1g}) = -a(5x; \text{B1g}), \tag{5.4}$$

$$a(1x; \text{B2g}) = -a(2x; \text{B2g}), \tag{5.5}$$

$$a(3x; \text{B2g}) = a(4x; \text{B2g}) = -a(5x; \text{B2g}) = -a(6x; \text{B2g}), \tag{5.6}$$

$$a(1x; \text{B3u}) = a(2x; \text{B3u}), \tag{5.7}$$

$$a(3x; \text{B3u}) = a(4x; \text{B3u}) = a(5x; \text{B3u}) = a(6x; \text{B3u}), \tag{5.8}$$

where a(ix; Γ)s are the LC-*Px*-AO coefficients for the *i*-atom (the serial number $i = 1$–6; as shown in figure 1) within the Γ (Γ = Au, B1g, B2g or B3u) irreducible representation. The relationship equations (5) depend on the characters of various representations according to the D2h point group and the phases. For the MOs with "pure" representation, these relationship equations are obviously. As for the MO with non-pure representation Γ, the corresponding equations are also true. On the other hand, the π-MO may be expressed as:

$$\Psi = a(1x)\Phi(1x) + a(2x)\Phi(2x) + a(3x)\Phi(3x) + a(4x)\Phi(4x)$$
$$+ a(5x)\Phi(5x) + a(6x)\Phi(6x), \tag{6}$$

where $a(ix)s$ represent the LCAO coefficients of the *i*-atomic ($i = 1\ldots6$) *Px*-orbital $\Phi(ix)$. The π-MOs belong to the fuzzy representation overlapped by the

Au, B1g, B2g, and B3u. From equation (5), we can get:

$$a(1x) = a(1x; \text{B3u}) + a(1x; \text{B2g}), \tag{7.1}$$

$$a(2x) = a(2x; \text{B3u}) + a(2x; \text{B2g}), \tag{7.2}$$

$$a(3x) = a(3x; \text{B3u}) + a(3x; \text{B2g}) + a(3x; \text{Au}) + a(3x; \text{B1g}), \tag{7.3}$$

$$a(4x) = a(4x; \text{B3u}) + a(4x; \text{B2g}) + a(4x; \text{Au}) + a(4x; \text{B1g}), \tag{7.4}$$

$$a(5x) = a(5x; \text{B3u}) + a(5x; \text{B2g}) + a(5x; \text{Au}) + a(5x; \text{B1g}), \tag{7.5}$$

$$a(6x) = a(6x; \text{B3u}) + a(6x; \text{B2g}) + a(6x; \text{Au}) + a(6x; \text{B1g}). \tag{7.6}$$

Further, by using equations (6) and (7) and primary algebra, we may obtain that:

$$a(1x; \text{B3u}) = a(2x; \text{B3u}) = [a(1x) + a(2x)]/2, \tag{8.1}$$

$$a(1x; \text{B2g}) = -a(2x; \text{B2g}) = [a(1x) - a(2x)]/2, \tag{8.2}$$

$$a(3x; \text{B3u}) = a(4x; \text{B3u}) = a(5x; \text{B3u}) = a(6x; \text{B3u})$$
$$= [a(3x) + a(4x) + a(5x) + a(6x)]/4, \tag{8.3}$$

$$a(3x; \text{B2g}) = a(4x; \text{B2g}) = -a(5x; \text{B2g}) = -a(6x; \text{B2g})$$
$$= [a(3x) + a(4x) - a(5x) - a(6x)]/4, \tag{8.4}$$

$$a(3x; \text{Au}) = -a(4x; \text{Au}) = a(5x; \text{Au}) = -a(6x; \text{Au})$$
$$= [a(3x) - a(4x) + a(5x) - a(6x)]/4, \tag{8.5}$$

$$a(3x; \text{B1g}) = -a(4x; \text{B1g}) = -a(5x; \text{B1g}) = a(6x; \text{B1g})$$
$$= [a(3x) - a(4x) - a(5x) + a(6x)]/4. \tag{8.6}$$

These results we can also get by means of projection operators [16]. Therefore, the irreducible representation compositions of these π-MOs may be calculated as follows:

$$X(\text{B3u}) = \Sigma[a^2(\text{B3u})]/\Sigma(a^2) = [a^2(1x; \text{B3u}) + a^2(2x; \text{B3u}) + a^2(3x; \text{B3u})$$
$$+ a^2(4x; \text{B3u}) + a^2(5x; \text{B3u})$$
$$+ a^2(6x; \text{B3u})]/\Sigma(a^2), \tag{9.1}$$

$$X(\text{B2g}) = \Sigma[a^2(\text{B2g})]/\Sigma(a^2) = [a^2(1x; \text{B2g}) + a^2(2x; \text{B2g}) + a^2(3x; \text{B2g})$$
$$+ a^2(4x; \text{B2g}) + a^2(5x; \text{B2g})$$
$$+ a^2(6x; \text{B2g})]/\Sigma(a^2), \tag{9.2}$$

$$X(\text{Au}) = \Sigma[a^2(\text{Au})]/\Sigma(a^2) = [a^2(3x; \text{Au}) + a^2(4x; \text{Au}) + a^2(5x; \text{Au})$$
$$+ a^2(6x; \text{Au})]/\Sigma(a^2), \tag{9.3}$$

$$X(\text{B1g}) = \Sigma[a^2(\text{B1g})]/\Sigma(a^2) = [a^2(3x; \text{B1g}) + a^2(4x; \text{B1g}) + a^2(5x; \text{B1g})$$
$$+ a^2(6x; \text{B1g})]/\Sigma(a^2), \tag{9.4}$$

where:

$$\Sigma(a^2) \quad \equiv a^2(1x) + a^2(2x) + a^2(3x) + a^2(4x) + a^2(5x) + a^2(6x). \qquad (10)$$

It is not difficult to prove that:

$$X(B3u) + X(B2g) + X(Au) + X(B1g) = 1. \qquad (11)$$

Now we turn to analyze the LCAO coefficients of σ-MO. For the four irreducible representations in relation to σ-MOs, all of the LC-Px-AOs coefficients vanish. The LC-S, Py, Pz-AO coefficients may be obtained by similar way of dealing with π-MOs. We may get the $a(is; \Gamma), a(iy; \Gamma)$, and $a(iz; \Gamma)$, where the atomic serial number $i = 1$–6, and the irreducible representation Γ = Ag, B1u, B2u or B3g. However since all kinds of the S, Py, Pz-AOs can affect the relative irreducible representation Γ, the calculation program for σ-MOs, should be similar to equation (9), which is in connection with various irreducible representations, Γ. Thus, we must consider the contribution of all the three kinds of S, Py, Pz-AOs to each irreducible representation. For the σ-MO, it may also prove that:

$$X(B3g) + X(B2u) + X(Ag) + X(B1u) = 1. \qquad (12)$$

As mentioned above, we can get the membership functions and representation compositions of relative molecules and MOs by the diverse and complicated but no objected calculation. The calculation will be simplified as we make it program.

3. Results and discussion

3.1. The molecular fuzzy symmetry of C2F3Cl

First, we analyze the fuzzy symmetry of C2F3Cl. In this molecule, a chlorine atom replaces one fluorine atom in ethylene tetra-fluoride. Except the molecular plane-mirror, the other twofold transformations in the D2h of ethylene tetra-fluoride molecule can not be conserved perfectly. However we can examine their corresponding molecular fuzzy symmetry. As shown in figure 1, the chlorine atomic serial number is '3'. Because the mirror Mx is the molecular plane, its relative symmetry is conserved perfectly, and the corresponding membership function is equal to 1. The membership functions of other twofold symmetry transformations may be calculated by using equation (1). If the atomic number Z is used as the criterion Y, the values of all these membership functions are 0.8571. According to the idea of Zadeh [17,18], the fuzzy point group of this

molecular skeleton can be written as:

$$\underset{\sim}{\mathbf{D_{2h}}} = \frac{1}{\hat{E}} + \frac{1}{\hat{M}x} + \frac{0.8571}{\hat{M}y} + \frac{0.8571}{\hat{M}z} + \frac{0.8571}{\hat{P}} + \frac{0.8571}{\hat{C}x} + \frac{0.8571}{\hat{C}y} + \frac{0.8571}{\hat{C}z},$$

(13)

where the $\hat{M}w$ and $\hat{C}w$ ($w =$ x, y, z) are the mirror reflection (w-axis as the normal) and the twofold rotation(W-axis as the rotation axis) transform operations, respectively. If the criterion Y is the electronic charge at atom, the membership functions will be varied a little, and the fuzzy point group (at AM1 level) of this molecular skeleton:

$$\underset{\sim}{\mathbf{D_{2h}}} = \frac{1}{\hat{E}} + \frac{1}{\hat{M}x} + \frac{0.8594}{\hat{M}y} + \frac{0.8553}{\hat{M}z} + \frac{0.8555}{\hat{P}} + \frac{0.8555}{\hat{C}x} + \frac{0.8553}{\hat{C}y} + \frac{0.8594}{\hat{C}z}$$

(14)

(cf. data in table 3). For the MOs of C_2F_3Cl, 24 MOs can be obtained from the combination of the AOs of the six atomic valence shells. For every MO, the membership functions and the irreducible representation compositions can be calculated. And then, we can get the corresponding fuzzy point group and fuzzy representation. For example, the fuzzy point group corresponding to the HOMO of C_2F_3Cl, may be expressed as:

$$\underset{\sim}{\mathbf{D_{2h}}} = \frac{1}{\hat{E}} + \frac{1}{\hat{M}x} + \frac{0.9462}{\hat{M}y} + \frac{0.8794}{\hat{M}z} + \frac{0.8794}{\hat{P}} + \frac{0.8794}{\hat{C}x} + \frac{0.8794}{\hat{C}y} + \frac{0.9462}{\hat{C}z}$$

(15)

(cf. data in table 2). Where the "numerators" are relative membership functions. And the fuzzy representation may be defined as:

$$\underset{\sim}{\mathbf{\Gamma}}(\text{HOMO}) = 0.9952B_{3u} + 0.0031B_{2g} + 0.0009A_u + 0.0008B_{1g}$$

(16)

(cf. data in table 1). The numbers before the irreducible representation symbols are corresponding irreducible representations compositions.

In table 1, the irreducible representation compositions of 24 MOs, which formed by the C_2F_3Cl valence-shell AOs, are listed. Using the data in table 1, it is not difficult to get the fuzzy representation expressions of 24 MOs of C_2F_3Cl molecule. These expressions are similar to equation (16). Further analysis of the MOs, we can be aware that as follows:

1 Though the MOs of C_2F_3Cl are not provided with the 'pure' irreducible representations in relation to the common D2h point group, but with the mixture of some irreducible representations. Among these irreducible representations, the one with the maximum composition may be called

Table 1

The various irreducible representation compositions of 24 MOs formed by the C2F3Cl valence-shell AOs (the order of the MO serial numbers is the same to the order of energy increase; where the MO-18 and the MO-19 are the HOMO and LVMO, respectively).

	Ag	B1u	B2u	B3g	B3u	B2g	Au	B1g
MO-1, σ	0.5751	0.4220	0.0014	0.0015	0	0	0	0
MO-2, σ	0.1704	0.2853	0.5237	0.0207	0	0	0	0
MO-3, σ	0.0390	0.0647	0.2069	0.6894	0	0	0	0
MO-4, σ	0.2111	0.2344	0.2586	0.2959	0	0	0	0
MO-5, σ	0.9198	0.0772	0.0016	0.0015	0	0	0	0
MO-6, σ	0.0109	0.9827	0.0032	0.0032	0	0	0	0
MO-7, σ	0.3125	0.0092	0.6574	0.0210	0	0	0	0
MO-8, σ	0.6689	0.0219	0.2897	0.0195	0	0	0	0
MO-9, π	0	0	0	0	0.8814	0.1008	0.0096	0.0082
MO-10, σ	0.0154	0.0319	0.0165	0.9363	0	0	0	0
MO-11, π	0	0	0	0	0.0567	0.7564	0.0816	0.1053
MO-12, σ	0.0783	0.7915	0.0622	0.0680	0	0	0	0
MO-13, π	0	0	0	0	< 0.0001	0.0010	0.4944	0.5045
MO-14, σ	0.0002	0.0003	0.5109	0.4885	0	0	0	0
MO-15, σ	0.6118	0.0108	0.1880	0.1894	0	0	0	0
MO-16, π	0	0	0	0	0.0766	0.1364	0.4101	0.3769
MO-17, σ	0.3654	0.1580	0.2137	0.2630	0	0	0	0
MO-18, π	0	0	0	0	0.9952	0.0031	0.0009	0.0007
MO-19, π	0	0	0	0	0.0009	0.9989	0.0001	< 0.0001
MO-20, σ	0.1386	0.6764	0.1132	0.0719	0	0	0	0
MO-21, σ	0.1619	0.7122	0.1038	0.0221	0	0	0	0
MO-22, σ	0.3257	0.1312	0.4665	0.0766	0	0	0	0
MO-23, σ	0.1296	0.7638	0.0113	0.0954	0	0	0	0
MO-24, σ	0.0083	0.2635	0.0022	0.7261	0	0	0	0

main irreducible representation. However, the cases for various MOs are quite different. Sometimes, some irreducible representation compositions are close to one. However, in other cases, may not be near by one. The frontier orbitals, HOMO and LVMO, are more 'pure', their main irreducible representation compositions may be quite close to one. Such phenomena appear not only in the C_2F_3Cl molecule, but also in some other molecules not a rare. For this reason, the frontier orbital theorem [19] may be in effect to un-perfect symmetry condition.

2 For C_2F_3Cl, the main irreducible representations (the compositions of these irreducible representations is maximum, but not only representation for each) of these 24 MOs as follows:

Occupied (Ag) (B2u) (B3g) (B3g) (Ag) (B1u) (B2u) (Ag) (B3u)
         (B3g) (B2g) (B1u) (B1g) (B2u) (Ag) (Au) (Ag) (B3u)
Virtual   (B2g) (B1u) (B1u) (B2u) (B1u) (B3g)

The occupied MOs are MO-1 to MO-18 and virtual MOs are MO-19 to MO-24, respectively.

Compared with the 24 irreducible representations ("pure" and "main", simultaneously) of the C_2F_4 MOs, although the energetic orders are somewhat different between the MOs of C_2F_3Cl and C_2F_4, the numbers of various irreducible representations are the same. From this, we can get the MO correlation diagram (figure 2). For each MO with a certain main irreducible representation in C_2F_3Cl, there is a corresponding MO with the same main (i.e. pure) irreducible representation in C_2F_4. Especially, for the frontier orbital, the near "pure" irreducible representation in C_2F_3Cl molecule and the "pure" irreducible representation in C_2F_4 molecule are the same.

3 The MOs in C_2F_3Cl provided the $\underset{\sim}{\mathbf{D_{2h}}}$ fuzzy point group symmetry. For

the related transformations in above fuzzy point group, the membership functions can be obtained for each MO, which are shown in table 2. It is noticed that here the membership functions of both the $\hat{E}$ and $\hat{M}x$ are always equal to 1, that ought to be true, for various planar molecule. From table 2, we can get the fuzzy point group expressions of 24 MOs in C_2F_3Cl molecule, which will be similar as equation (15) in form.

It also can be seen from table 2 that the membership functions of frontier orbitals are somewhat near by one. For various symmetry transformations, the membership functions are different. It seems that there is some relationship between the irreducible representation compositions and membership functions. As a few reduction of irreducible representation compositions, the membership function will be changed in various effects, similar to the case of the linear molecule [8].

4 The correlation diagram, as shown in figure 2, can be called fuzzy correlation diagram. It differs somewhat from common MO correlation diagram. The differences between them are as follows: first of all, in the common MO correlation diagram, the symmetries between MOs are either the same or not the same. All the correlation lines are equi-weight, and the corresponding symmetries between MOs linked by a correlation line are the same. If the symmetries are not the same, the MOs can not be linked by a correlation line. However for the molecular fuzzy symmetry, the symmetries may be partial but not whole the same. It means that the membership functions and the representations compositions relative to the symmetries may be a certain value between the 0 and 1, while in a common MO correlation diagram, they are either 0 or 1. All of the MO representation compositions in C_2F_4 are 1, but those in C_2F_3Cl are between 0 and 1. Therefore, the correlation degree of various correlation lines may be different. Moreover, one MO may be correlated with

C2F4			C2F3Cl	
MO	(Eigenvalues) 'pure' irreducible representations		main irreducible representations (Eigenvalues)	MO
MO-24, σ	(0.15825) B3g		B3g (0.15540)	MO-24, σ
MO-23, σ	(0.14536) B1u		B1u (0.14041)	MO-23, σ
MO-22, σ	(0.11132) Ag		B2u (0.10463)	MO-22, σ
MO-21, σ	(0.09566) B2u		B1u (0.06054)	MO-21, σ
MO-20, σ	(0.02748) B1u		B1u(-0.00113)	MO-20, σ
MO-19, π	(-0.02418) B2g		B2g(-0.02196)	MO-19, π
MO-18, π	(-0.37433) B3u		B3u(-0.37092)	MO-18, π
MO-17, σ	(-0.53479) Ag		Ag (-0.47738)	MO-17, σ
MO-16, σ	(-0.56220) B2u		Au (-0.49993)	MO-16, π
MO-15, σ	(-0.56256) B3g		Ag (-0.52120)	MO-15, σ
MO-14, π	(-0.57818) Au		B2u(-0.55966)	MO-14, σ
MO-13, π	(-0.58078) B1g		B1g(-0.57717)	MO-13, π
MO-12, σ	(-0.60440) B1u		B1u(-0.58475)	MO-12, σ
MO-11, π	(-0.64426) B2g		B2g(-0.61833)	MO-11, π
MO-10, σ	(-0.67149) B3g		B3g(-0.65004)	MO-10, σ
MO-9, π	(-0.70578) B3u		B3u(-0.68852)	MO-9, π
MO-8, σ	(-0.74323) B2u		Ag (-0.73032)	MO-8, σ
MO-7, σ	(-0.75519) Ag		B2u(-0.73863)	MO-7, σ
MO-6, σ	(-0.87654) B1u		B1u(-0.87268)	MO-6, σ
MO-5, σ	(-1.17492) Ag		Ag (-1.17643)	MO-5, σ
MO-4, σ	(-1.81284) B3g		B3g(-1.42129)	MO-4, σ
MO-3, σ	(-1.85369) B2u		B3g(-1.82293)	MO-3, σ
MO-2, σ	(-1.90380) B1u		B2u(-1.86264)	MO-2, σ
MO-1, σ	(-1.91139) Ag		Ag (-1.90878)	MO-1, σ

Figure 2. MO fuzzy correlation diagram between C2F4 and C2F3Cl.

more MOs, but only the main correlation lines are shown in figure 2. On the other hand, for the common correlation diagram, the correlation lines usually are introduced according to only one symmetrical property (symmetry or asymmetry) of only one certain transformation. Just as the analysis of the electrocyclic reaction by using the W-Hrule [13,14], for the conrotatory and disrotatory mechanisms, the corresponding correlation diagrams [20] are based on twofold rotation and mirror reflection

Table 2

The membership functions in relation to various symmetry transformations of 24 MOs formed by the C2F3Cl valence-shell AOs (the order of the MO serial numbers is the same to the order of energy increase; where the MO-18 and MO-19 are the HOMO and LVMO, respectively).

MO	$\hat{P}$ & $\hat{C}x$	$\hat{M}z$ & $\hat{C}y$	$\hat{M}y$ & $\hat{C}z$	$\hat{M}x$ & $\hat{E}$
MO-1, σ	0.0178	0.0178	0.9897	1
MO-2, σ	0.2642	0.1147	0.1658	1
MO-3, σ	0.3158	0.3161	0.7666	1
MO-4, σ	0.0176	0.0084	0.0422	1
MO-5, σ	0.9208	0.8934	0.9751	1
MO-6, σ	0.8165	0.8165	0.9309	1
MO-7, σ	0.5096	0.7135	0.5590	1
MO-8, σ	0.5102	0.7772	0.4583	1
MO-9, π	0.3816	0.3816	0.8313	1
MO-10, σ	0.5861	0.6588	0.6904	1
MO-11, π	0.3217	0.2703	0.3425	1
MO-12, σ	0.4424	0.4491	0.7061	1
MO-13, π	0.0123	0.0123	0.9647	1
MO-14, σ	0.0014	0.0014	0.9888	1
MO-15, σ	0.3341	0.3837	0.6168	1
MO-16, π	0.0521	0.0521	0.3537	1
MO-17, σ	0.0574	0.0347	0.0978	1
MO-18, π	0.8794	0.8794	0.9462	1
MO-19, π	0.9410	0.9410	0.9902	1
MO-20, σ	0.2867	0.2410	0.6477	1
MO-21, σ	0.3436	0.3525	0.8755	1
MO-22, σ	0.3695	0.6726	0.6014	1
MO-23, σ	0.3534	0.3472	0.8594	1
MO-24, σ	0.7032	0.8439	0.7843	1

symmetry transformations, respectively, but not on the C$_{2v}$ point group at whole. Just as mentioned above in figure 2, the MOs linked by a correlation lines are only for the MOs with the same main irreducible representations. It means that the MOs linked by one correlation line ought to be with the same characters for all symmetry transformations in relation to the D2h point group. Of course, for such correlation line we may also only introduce a certain symmetry transformation or a certain subgroup of D2h point group to correlate them. As regards the fuzzy correlation diagram, the general characterization and application to relative processes will be analyzed in our follow-up papers.

5 By the way, according to the conditions of fuzzy subgroup [4,21], in relation to D2h group for the C$_2$F$_3$Cl molecular skeleton and MOs, the corresponding fuzzy symmetry transformation sets sometimes only the fuzzy sets but not the fuzzy subgroups. For example, if based on the

Table 3
The membership functions in relation to various symmetry transformations of C2F3X (X=F,Cl,Br,I) molecule skeletons.

C2F3X	$\hat{P}$ & $\hat{C}x$	$\hat{M}z$ & $\hat{C}y$	$\hat{M}y$ & $\hat{C}z$	$\hat{M}x$ & $\hat{E}$
C2F4(Z)	1	1	1	1
C2F4(E)	1	1	1	1
C2F3Cl(Z)	0.8571	0.8571	0.8571	1
C2F3Cl(E)	0.8555	0.8553	0.8594	1
C2F3Br(Z)	0.6487	0.6487	0.6487	1
C2F3Br(E)	0.6468	0.6466	0.6515	1
C2F3I(Z)	0.5217	0.5217	0.5217	1
C2F3I(E)	0.5204	0.5203	0.5253	1

The Z and E in brackets following the molecular formulae imply that the membership functions are calculated based on the atomic number and the electronic charge (at AM1 level) as the atomic criteria(Y), respectively.

atomic number as the atomic criteria (Y) for C_2F_3Cl molecular skeleton (table 3), the fuzzy symmetry transformation set in relation to D2h group may be the fuzzy subgroup, however if based on the electronic charge, it ought to be fuzzy set but not fuzzy subgroup. As for C_2F_3Cl MOs (table 2), some of them are not fuzzy subgroup, yet.

We must note that, although both the membership functions and the representation compositions in MO are closely related and both with the values between 0 to 1, they are different concepts, just as the symmetry and the invariable belong to the categories of point group symmetry operation and point group representation, respectively [11].

3.2. The molecular fuzzy symmetries of C_2F_3Br and C_2F_3I

For the C_2F_3Br and C_2F_3I, we may analyze their molecular fuzzy symmetries as we do for C_2F_3Cl. The atomic serial number and space axes are shown still as Figure 1.

Both the Br and I atomic serial numbers are '3'. The membership functions corresponding to various symmetry transformations included in D2h point group relative to these molecule skeletons are shown in table 3. Since all these molecules are planar, all the values in the last column are equal to 1. It is conceivable that only if the λs are less than about 0.85, 0.64, and 0.52, for C_2F_3X with $X =$ Cl, Br and I, respectively, the λ-cut sets of their skeletons will be the D2h point group. Otherwise, they ought to be various subgroups of D2h.

As shown in table 3, for the C_2F_3X molecules, the bigger the size of X, the less the symmetry, i.e. the less the membership function. Thus it will affect on the MO symmetry. According to the method as mentioned above, the 24 MOs of various C_2F_3X molecules are analyzed. We can get the irreducible representation compositions for the fuzzy representation of every MO and the membership functions for every symmetry transformation in relation to D2h point group. And then we can get some interesting information as follows:

(1) For C_2F_3X (X = Br and I) molecules, the main irreducible representations of these 24 MOs are as follows:

    C_2F_3Br: Occupied (Ag) (B2u) (B3g) (Ag) (Ag) (B1u) (B2u) (Ag) (B3u)
                       (B3g) (B2g) (B1u) (Au) (B2u) (Ag) (Au) (B3g) (B3u)
                         Virtual (B2g) (B1u) (B1u) (B2u) (B1u) (B3g)

    C_2F_3I: Occupied (Ag) (B2u) (B3g) (Ag) (Ag) (B1u) (B2u) (Ag) (B3u)
                       (B3g) (B2g) (B1u) (Au) (B3g) (Ag) (Au) (B3g) (B3u)
                         Virtual (B1u) (B2g) (B1u) (B2u) (B1u) (B3g)

The occupied MOs are MO-1 to MO-18 and virtual MOs are MO-19 to MO-24, respectively.

(2) For the HOMO(MO-18)s of C_2F_4, C_2F_3Cl, C_2F_3Br, and C_2F_3I, the main irreducible representations of all the HOMO(MO-18)s are B3u. The corresponding representation compositions are all more then 0.98, and it is 1 for the main and pure representation of C_2F_4. For the LVMO(MO-19)s of the C_2F_4, C_2F_3Cl, and C_2F_3Br molecules, the main irreducible representations are B2g, and the corresponding representation compositions are more than 0.99. However, for C_2F_3I molecule, the MO corresponding to the main irreducible representation B2g moves from LVMO to next-LVMO, although its representation composition is still more than 0.99.

(3) If we draw up the correlation diagram between the C_2F_3Br and C_2F_4 as we do so for C_2F_3Cl and C_2F_4, it will be found that their main irreducible representations could not be matched perfectly. For the MOs of C_2F_3Br, a main irreducible representation, Au, will be remained to correlate with the B1g main (pure) irreducible representation remained in C_2F_4. For the MO-13 in C_2F_3Br, its main irreducible representation is Au, and its next-main irreducible representation is B1g, moreover these two irreducible representation compositions are 0.5078 and 0.4902, respectively, they are close on. Therefore this MO with the next-main (but not with main) irreducible representation to correlate the MO remained in C_2F_4 with main and pure irreducible representation B1g ought to be reasonable.

(4) For the correlation diagram between the C_2F_3I and C_2F_4 based on the main irreducible representations, not only the MO-13 ought to be with its next-main irreducible representation B1g (its composition about 0.48) to correlate with the MO in C_2F_4, but also the MO-14 ought to be its next-main irreducible representation B2u to replace the main irreducible representation B3g and to correlate with the MO in C_2F_4. These two irreducible representation compositions are 0.4947 and 0.5010, respectively. They are also close on.

(5) As analyzed above, although all these MOs in these molecules according to their main or next-main irreducible representations may correlate with the MOs in C_2F_4 according to common irreducible representation in D2h point group and may be established the correlation diagrams by such way. However the symmetry perfection of molecular skeleton will be weakened, i.e. the membership functions reduced, progressively in order of C_2F_3Cl, C_2F_3Br, and C_2F_3I. The symmetry for single MO may be changed with different way, but the correlation for D2h point group between the MO sets of these molecules and C_2F_4 will be weakened in order mentioned-above. When we establish the corresponding correlation diagram, the next-main irreducible representation will be introduced in more times.

(6) As mentioned above, we can get the MO correlation diagrams between C_2F_4 and C_2F_3X (X = Cl, Br or I), as shown in figure 3. In this figure the correlation lines are drawn based on the correlation of the main (some on the next-main) irreducible representations. Of course, the σ-MO will be correlated with the σ-MO only (so-called the σ-correlation line), and π-MO will be correlated with the π-MO only (so-called the π-correlation line). As shown in figure 3, the π-correlation lines are not crossed each other. It means that the characterization relative to symmetrical control process for the π-MO symmetry ought to be similar. As shown in figure 3, for the correlation lines between the MOs of C_2F_4 and C_2F_3X (X=Cl, Br or I), some correlation lines may cross the non-bonding level, but for the correlation lines between the MOs of different C_2F_3X ($X \neq F$), all the correlation lines do not cross the non-bonding level. It may be predicted that the characterization relative to symmetrical control process for these C_2F_3X ought to be more similar.

(7) It is noteworthy that the characterizations of correlations between the MOs of various C_2F_3X ($X \neq F$) and between the MOs of C_2F_4 and one of the C_2F_3X ($X \neq F$) are different. In the former case, the MOs linked by the correlation lines, the relative representations are both fuzzy for the D2h point group, and the main representation compositions are less than 1, the correlation degree of the MOs will be determined by both

Main representations

	C2F4	C2F3Cl	C2F3Br	C2F3I
MO-24, σ	B3g	B3g	B3g	B3g
MO-23, σ	B1u	B1u	B1u	B1u
MO-22, σ	Ag	B2u	B2u	B2u
MO-21, σ	B2u	B1u	B1u	B1u
MO-20, σ	B1u	B1u	B1u	B2g
MO-19, π	B2g	B2g	B2g	B1u
MO-18, π	B3u	B3u	B3u	B3u
MO-17, σ	Ag	Ag	B3g	B3g
MO-16, σ	B2u	Au	Au	Au
MO-15, σ	B3g	Ag	Ag	Ag
MO-14, π	Au	B2u	B2u	B3g**
MO-13, π	B1g	B1g	Au*	Au*
MO-12, σ	B1u	B1u	B1u	B1u
MO-11, π	B2g	B2g	B2g	B2g
MO-10, σ	B3g	B3g	B3g	B3g
MO-9, π	B3u	B3u	B3u	B3u
MO-8, σ	B2u	Ag	Ag	Ag
MO-7, σ	Ag	B2u	B2u	B2u
MO-6, σ	B1u	B1u	B1u	B1u
MO-5, σ	Ag	Ag	Ag	Ag
MO-4, σ	B3g	B3g	Ag	Ag
MO-3, σ	B2u	B3g	B3g	B3g
MO-2, σ	B1u	B2u	B2u	B2u
MO-1, σ	Ag	Ag	Ag	Ag

Figure 3. MO fuzzy correlation diagram between C2F4, C2F3Cl, C2F3Br and C2F3I. (**according to the next-main irreducible representation B2u; *according to the next-main irreducible representation B1g).

these two fuzzy symmetries of C_2F_3X ($X \neq F$) MOs. In the latter case, the main- (i.e. pure-) representation compositions for C_2F_4 are equal to 1, the correlation degree of the MOs will be only determined by the MO fuzzy symmetry of C_2F_3X ($X \neq F$). As a certain MO with the poor main representation compositions, the correlation degree of related line will be poor, too. For instances, both the MO-4 of C_2F_3Cl and the MO-17 of C_2F_3Br, their main representation compositions are

Main representations

	C2F4	C2F3Cl	C2F3Br	C2F3I
MO-24, σ	B3g	B3g	B3g	B3g
MO-23, σ	B1u	B1u	B1u	B1u
MO-22, σ	Ag	B2u	B2u	B2u
MO-21, σ	B2u	B1u	B1u	B1u
MO-20, σ	B1u	B1u	B1u	B2g
MO-19, π	B2g	B2g	B2g	B1u
MO-18, π	B3u	B3u	B3u	B3u
MO-17, σ	Ag	Ag	B3g	B3g
MO-16, σ	B2u	Au	Au	Au
MO-15, σ	B3g	Ag	Ag	Ag
MO-14, π	Au	B2u	B2u	B3g**
MO-13, π	B1g	B1g	Au*	Au*
MO-12, σ	B1u	B1u	B1u	B1u
MO-11, π	B2g	B2g	B2g	B2g
MO-10, σ	B3g	B3g	B3g	B3g
MO-9, π	B3u	B3u	B3u	B3u
MO-8, σ	B2u	Ag	Ag	Ag
MO-7, σ	Ag	B2u	B2u	B2u
MO-6, σ	B1u	B1u	B1u	B1u
MO-5, σ	Ag	Ag	Ag	Ag
MO-4, σ	B3g	B3g	Ag	Ag
MO-3, σ	B2u	B3g	B3g	B3g
MO-2, σ	B1u	B2u	B2u	B2u
MO-1, σ	Ag	Ag	Ag	Ag

Figure 4. MO fuzzy correlation (modified) diagram between C2F4, C2F3Cl, C2F3Br and C2F3I. (**according to the next-main irreducible representation B2u; *according to the next-main irreducible representation B1g).

about 0.30, merely. For such MO, sometimes, it may be correlated to the MO of other molecule with non-main representation. In fact, in such cases, not only one representation of each MO can be correlated to other one. Such correlation lines are designated as dotted lines as shown figure 4, and called it the MO fuzzy correlation (modified) diagram.

(8) Now we examine the correlation between the MOs of C_2F_3Cl and C_2F_3Br from figure 4. Because the MO-4(main representation B3g) of C_2F_3Cl correlates with the MO-4(main representation Ag) of C_2F_3Br, meanwhile, the MO-17 (main representation Ag) of C_2F_3Cl correlates with the MO-17 (main representation B3g) of C_2F_3Br, the correlation relationship between the MOs of C_2F_3Cl and C_2F_3Br ought to be matched on the whole. Moreover, all of the correlation lines are not cross, which means that the MOs of these two molecules may match perfectly at the fuzzy symmetry level.

(9) Certainly, for the MOs of the C_2F_3X (X = Cl, Br, and I), we can get their membership functions for the symmetry transformations in relation to the D2h point group. The results similar to the data in table 2 for those of C_2F_3Cl. Owing to the intrinsic molecular plan property, corresponding to the last column in table 2, all of the membership functions equal to 1. While other membership functions ought to be between 0 and 1. For various MOs and various symmetry transformations, the values of membership functions are very different. And the order for membership functions for MOs and that of the F, Cl, Br, and I for the molecule skeletons are not consistent. This is similar to the case of the diatomic molecules HX (X = F, Cl, Br, and I) [6, 8].

3.3. The molecular fuzzy symmetry of three $C_2F_2Cl_2$ isomers

Where three $C_2F_2Cl_2$ isomers to be addressed are *cis*-, *trans* $-$ CFCl $=$ CFCl and $CF_2 = CCl_2$. Their atomic serial numbers and the coordinate direction are show as same as figure 1. The serial number of one Cl atom is '3'. Follow this way, other atomic serial numbers may be defined accordingly. The symmetry rel-

Table 4
The membership functions in relation to various symmetry transformations of three C2F2Cl2 isomers molecule skeletons.

C2F2Cl2	$\hat{P}$ & $\hat{C}x$	$\hat{M}z$ & $\hat{C}y$	$\hat{M}y$ & $\hat{C}z$	$\hat{M}x$ & $\hat{E}$
CF2CCl2 (*Z*)	0.7500	0.7500	1	1
CF2CCl2 (*E*)	0.7480	0.7480	1	1
cis-C2F2Cl2(*Z*)	0.7500	1	0.7500	1
cis-C2F2Cl2(*E*)	0.7540	1	0.7540	1
trans-C2F2Cl2(*Z*)	1	0.7500	0.7500	1
trans-C2F2Cl2(*E*)	1	0.7536	0.7536	1

The Z and E in brackets following the molecular formulae denoted that the membership function are obtained based on the atomic number and the electronic charge (at AM1 level) as the atomic criteria(Y), respectively.

ative to mirror Mx (the x-axis direction is the normal direction, this mirror is also the molecular plane) ought to be perfect, and the corresponding membership function equals 1. The membership functions of other twofold symmetry transformations may be obtained according to the equation (1). We can treat these three isomers by the way similar to that for C_2F_3Cl. But, the results for these isomers are some different from those for C_2F_3Cl. As shown in table 4, in additional to the mirror Mx, there are some other twofold symmetry transformations still set up. Certainly, such two fold symmetry transformations are different for these three isomers. As shown in table 4, in additional to the values in the last column, which are equal 1 owing to be the molecular plane, the membership functions in one of other different column are also to 1 for each kind isomer. And the rest membership functions in other columns are between the 0 and 1. It means that a certain different symmetry of common subgroup which belongs to the D2h point group would be in each isomer molecule skeleton. And when the λ is less than 0.75, the λ-cut sets for these three kinds of isomer molecule skeletons will be the D2h point group, otherwise they will be the different subgroups of the D2h point group.

Of course, by the way for C_2F_3X as mentioned above, we may analyze the MOs of these three isomers. Some interesting information as follows:

(1) As the example, the irreducible representation compositions relative to the D2h point group for the 24 MOs in CF_2CCl_2 are show in table 5. Similar to the 24 MOs in C_2F_3X (X=Cl, Br or I), there are also 18σ-MOs and 6π-MOs still in these 24 MOs in CF_2CCl_2. Moreover, the representations are the Ag, B1u, B2u, and B3g for σ-MOs and those are the Au, B1g, B2g, and B3u for π-MOs. Different from a certain MO in C_2F_3X, which includes four representation compositions, a certain MO in CF_2CCl_2 includes only two representation compositions. Accordingly, the σ-MOs in CF_2CCl_2 can be classed into two kinds, one kind includes the (Ag,B1u) composition and the other includes the (B2u,B3g) one, respectively. Similarly, the two kinds of π-MOs include the (Au,B1g) and (B2g,B3u) ones, respectively. There are not four representation compositions include in one MO, simultaneously. Evidently, that is the effects owing to the CF_2CCl_2 molecule providing with the symmetry of a certain common subgroups of D2h.

(2) The symmetry of the other two isomers are similar to that of CF_2CCl_2. Each MO includes only two representation compositions, in general. For the σ-MOs in *cis*-$C_2F_2Cl_2$, the two kinds of σ-MOs include the (Ag,B2u) and (B1u,B3g). And for the π-MO there are the (Au,B2g) and (B1g,B3u), respectively. While for *trans*-$C_2F_2Cl_2$, the kinds of σ-MOs are the (Ag,B3g) and (B2u,B1u), and the kinds of π-MOs are the (Au,B3u) and (B2g,B1g), respectively. There is not any one MO, which includes four representation compositions, simultaneously. Since

Table 5
The various irreducible representation compositions of 24 MOs formed by the CF2CCl2 valence-shell AOs (the order of the MO serial numbers is the same to the order of energy increase; where the MO-18 and MO-19 are the HOMO and LVMO, respectively).

	Ag	B1u	B2u	B3g	B3u	B2g	Au	B1g
MO-1, σ	0.5187	0.4813	0	0	0	0	0	0
MO-2, σ	0	0	0.5226	0.4774	0	0	0	0
MO-3, σ	0.4758	0.5242	0	0	0	0	0	0
MO-4, σ	0	0	0.4682	0.5318	0	0	0	0
MO-5, σ	0.7959	0.2041	0	0	0	0	0	0
MO-6, σ	0.0297	0.9703	0	0	0	0	0	0
MO-7, σ	0	0	0.8975	0.1025	0	0	0	0
MO-8, σ	0.9213	0.0787	0	0	0	0	0	0
MO-9, π	0	0	0	0	0.7466	0.2534	0	0
MO-10, σ	0	0	0.0833	0.9167	0	0	0	0
MO-11, π	0	0	0	0	0	0	0.4820	0.5180
MO-12, σ	0.3488	0.6512	0	0	0	0	0	0
MO-13, σ	0	0	0.5292	0.4708	0	0	0	0
MO-14, π	0	0	0	0	0.2799	0.7201	0	0
MO-15, σ	0.7265	0.2735	0	0	0	0	0	0
MO-16, π	0	0	0	0	0	0	0.5193	0.4807
MO-17, σ	0	0	0.4686	0.5314	0	0	0	0
MO-18, π	0	0	0	0	0.9896	0.0104	0	0
MO-19, π	0	0	0	0	0.0023	0.9977	0	0
MO-20, σ	0.2325	0.7675	0	0	0	0	0	0
MO-21, σ	0	0	0.7056	0.2944	0	0	0	0
MO-22, σ	0.3262	0.6738	0	0	0	0	0	0
MO-23, σ	0	0	0.1456	0.8544	0	0	0	0
MO-24, σ	0.1187	0.8813	0	0	0	0	0	0

the subgroups of D2h point group, which each isomer molecular skeletons belong to are different, the combination ways of MO representations for various isomers are different, too.

(3) Similar to those of C_2F_3Cl, the representations of the frontier MOs for these three isomer molecules provide the more pure π-MOs. Their representation compositions are more than 0.99 in general.

(4) For these three isomers, the main irreducible representations of these 24 MOs are as follows:

CF_2CCl_2: Occupied   (Ag) (B2u) (B1u) (B3g) (Ag) (B1u) (B2u) (Ag) (B3u) (B3g) (B1g) (B1u) (B2u) (B2g) (Ag) (Au) (B3g) (B3u)
         Virtual (B2g) (B1u) (B2u) (B1u) (B3g) (B1u)

cis-$C_2F_2Cl_2$Occupied   (Ag) (B1u) (B2u) (B3g) (Ag) (B1u) (B2u) (Ag)
(B3u) (B3g) (B2g) (B1u) (B2u) (B1g) (Au) (Ag) (B3g) (B3u)
Virtual (B2g) (B1u) (Ag) (B1u) (Ag) (B3g)
trans-$C_2F_2Cl_2$Occupied (B1u) (Ag) (B3g) (B2u) (Ag) (B1u) (B2u) (Ag)
(B3u) (B3g) (B2g) (B1u) (B3g) (Au) (B1g) (B2u) (Ag) (B3u)
Virtual (B2g) (B1u) (Ag) (B1u) (B1u) (B3g)

The occupied MOs are MO-1 to MO-18 and virtual MOs are MO-19 to MO-24, respectively.

Compared with the main (i.e. pure) irreducible representations of the 24 MOs of the C_2F_4, one of the MO in CF_2CCl_2 with main representation B1u ought to be using the next-main representation Ag to correlate the corresponding MO in C_2F_4. One of the MO in *cis*-$C_2F_2Cl_2$ with main representation Ag ought to be using the next-main representation B2u to correlate the corresponding MO in C_2F_4. One of the MO in *trans*-$C_2F_2Cl_2$ with main representation B1u ought to be using the next-main representation B2u to correlate the corresponding MO in C_2F_4. For these three isomers, there are such MOs, these MOs may be satisfied such conditions for the match of representation, meanwhile the values of main and next-main representation compositions difference are not too much. It is not difficult to get the correlation diagrams between the MOs of the C_2F_4 and each of the isomer. In these diagrams, there are more crosses between the correlation lines. Owing to there only two irreducible representations included in the isomer MO, all the main representation compositions must be more than 0.5 (could not too small), the correlation dotted lines as shown in figure 4 can not appeared.

(5) Certainly, for the MOs of these isomers we can get their membership functions of the symmetry transformations in relation to the D2h point group. Owing to the symmetries of molecule skeleton and the MOs are related to each other, for the symmetry transformations with the membership function equal one in table 4, the membership functions in relation to such symmetry transformations for MOs ought to be provided with the membership function still equal one. Meanwhile, for the symmetry transformations with the membership function not equal one in table 4, the membership functions in relation to such symmetry transformations for MOs ought to be provided with the membership function not equal one, too, but the values of the membership functions for various MOs ought to be different, as shown in table 6 (the values of membership function equal one are omitted).

Table 6

The membership functions in relation to various symmetry transformations of 24 MOs formed by the C2F2Cl2 isomer valence-shell AOs (the order of the MO serial numbers is the same to the order of energy increase; where the MO-18 and MO-19 are the HOMO and LVMO, respectively).

	CF2CCl2	*cis*-C2F2Cl2	*trans*-C2F2Cl2
	$\hat{P}, \hat{C}x, \hat{M}z \& \hat{C}y$	$\hat{P}, \hat{C}x, \hat{M}y \& \hat{C}z$	$\hat{M}z, \hat{C}y, \hat{M}y \& \hat{C}z$
MO-1	0.0022	0.0840	0.0632
MO-2	0.0012	0.0628	0.0866
MO-3	0.0201	0.0714	0.0740
MO-4	0.0024	0.0224	0.0183
MO-5	0.3254	0.9505	0.9973
MO-6	0.6931	0.8055	0.8377
MO-7	0.3846	0.6939	0.6492
MO-8	0.7877	0.3989	0.6491
MO-9	0.1247	0.4034	0.3996
MO-10	0.5362	0.4937	0.6611
MO-11	0.0007	0.1328	0.1174
MO-12	0.2286	0.7215	0.2642
MO-13	0.0019	0.5217	0.5165
MO-14	0.2772	0.5913	0.5997
MO-15	0.1478	0.1356	0.1171
MO-16	0.0007	0.3702	0.0871
MO-17	0.0024	0.3302	0.1122
MO-18	0.7854	0.9187	0.9058
MO-19	0.9065	0.9790	0.9771
MO-20	0.2511	0.8943	0.5739
MO-21	0.1087	0.8691	0.6399
MO-22	0.1950	0.9701	0.8404
MO-23	0.2855	0.5609	0.8885
MO-24	0.3975	0.7561	0.6905

4.   Conclusions

Based on our pervious study in relation to the fuzzy symmetry characterization and the application to linear molecule, the fuzzy symmetry of the planar molecule have been analyzed, in this paper. The prototypical planar molecules we have chosen to probe are C_2F_3X (*X*=Cl, Br, and I) and three kinds of $C_2F_2Cl_2$ isomers. The symmetry of these molecules relates to the fuzzy set in connection with the D2h point group. As we known, the D2h point group includes several twofold symmetry transformations but without higherfold one. It may be related to some one-dimensional irreducible representations but not to multi-dimensional irreducible representations. In this paper, the fuzzy symmetries of these molecules and their MOs have been studied. The membership functions,

the representation compositions, the fuzzy correlation diagrams and so on have been obtained. It is expected that these analysis methods ought to be extended to the analysis of the molecular fuzzy symmetries for some other molecule systems as follows:

(1) According to the elementary characterization of molecular fuzzy symmetry, the computational methods of the membership functions and the irreducible representation compositions in relation to the D2h point group for the ethylene tetra-halide molecules and their MO are announced, in this paper.

(2) For these reflection symmetry transformations in relation to the molecular plane as a mirror, the membership functions of both the skeletons and their MOs are equal to one. For the other twofold symmetry transformations, both the membership functions of the skeletons and of their MOs are between the 0 and 1. With the membership functions, we may get the Zadeh expressions of both the molecular skeletons and their MOs in relation to the fuzzy symmetry.

(3) For these molecules, the fuzzy representation of each MO may be overlapped with no more than four irreducible representation compositions belonging to D2h point group, and then we can get the fuzzy representation expression (16). The representations included are the Ag, B1u, B2u, and B3g in σ-MOs, and the Au, B1g, B2g, and B3u in π-MO. In each MO, the summation of various representation compositions equals one.

(4) The fuzzy representation of each MO in C_2F_3X (X = Cl, Br or I) would be the results of the overlap of four irreducible representation compositions in D2h point group. Every representation composition depends on the X-atom in relative molecule skeleton and more important on the characterization of MO. For example, each of these MO only related to four of eight representations in D2h point group and other four representation compositions will be null. Which four will be null, depends on the type of the MO, σ or π.

(5) Corresponding to the maximum composition in each MO, the representation can be called main-representation. Through the main-representations, sometimes the next- main representations, we can constitute the fuzzy correlation diagram between the MOs of C_2F_3X (X = Cl, Br or I) and C_2F_4 in relation to the D2h point group.

(6) For three $C_2F_2Cl_2$ isomer molecules (CF_2CCl_2, *cis*-$C_2F_2Cl_2$, and *trans*-$C_2F_2Cl_2$), in addition to the reflection symmetry transformation with the molecular plane as a mirror, there are several other twofold symmetry transformations. For some of them, the relative membership functions are

equal to one. Such transformations are different for various isomers, i.e. there common subgroup symmetries are different for these three isomers.

(7) For these three $C_2F_2Cl_2$ isomers, the fuzzy representation of each MO includes only two irreducible representations in relation to the D2h point group. The way of the combination two irreducible representations are different for various isomers. The frontier orbitals of these isomers are almost "pure" π-MOs.

Acknowledgments

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