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THEORETICAL STUDIES ON THE DISTRIBUTION OF THE DAUGHTER FRAGMENTS PRODUCED BY THE β^+-DECAY IN ^{18}F-LABELLED METHYLFLUORIDE

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The β^+-decay in $CH_3{}^{18}F$ was theoretically studied with ab initio MO calculation. The transition probability from a parent to the daughter in the ground and various excited states was calculated. The recoil effect as well as the electron shake-off will play an important role for the final products.

The transformed daughter and its fragmentation after the β^--decay have been extensively studied by both experimental and theoretical methods.1) However, the β^+-decay in molecule was experimentally studied only in $CH_3{}^{18}F$,2) and its interpretation has not been successfully done.

The present author has recently reported the theoretical studies on the β^--decay in $CH_3{}^3H$, $NH_2{}^3H$, OH^3H, $^{14}CH_4$, $^3HH_2N$---H-NH_2, and ^3H-cytosine1-b) using an ab initio MO calculation. The shape of the potential energy curves in the ground state daughter determines the main products following the β^--decay.

In this letter, the β^+-decay in $CH_3{}^{18}F$ will be studied using the same theoretical method already reported,1-b) and it will be shown that the recoil effect by β^+-ray as well as the electron shake-off will play an important role for the final products.

In sudden approximation, the transition probability (P_{gm}) from a parent to the daughter in the m-state is given as a square of the overlap matrix:$P_{gm}=[\langle\Phi_g|\Phi_m\rangle]^2$, between the electronic wavefunctions (Φ_g and Φ_m) of the parent and of the state m of the daughter.

An ab initio LCAO-SCF-MO method was used for the calculation of the wavefunctions of parent and the daughter in the various energy states. The hole potential method,3) equivalent to the improved virtual orbital method4) and equivalent to the Huzinaga-Arnau potential,5) was used for the calculation of the excited state daughter.

Huzinaga's Gaussian set (9s5p/4s)6) with Dunning contraction [5s3p/3s]7) was augmented with diffuse three s- and two p-Gaussian functions (ζ_s=0.08, 0.02, and 0.005; ζ_p=0.05 and 0.0125 8)) for the first row atoms.

These calculation methods and the basis set were already found to be very useful for the description of the ground and excited states. And it was also found that the electron correlation does not play an important role for the calculation of the transition probability, if the wavefunctions calculated with a fully extended basis set are used.1-b)

For the calculation the geometry of parent experimentally observed9) was used.

Throughout the study, ab initio calculations were performed with the RIKEN edition of QCPE Gaussian 70 on FACOM 230-75.

Table 1. Orbital and total energy in the ground state parent and daughter.

Orbital	Parent ($CH_3{}^{18}F$)			Daughter (CH_3O^-)			
	Orbital energy (a.u.)			Orbital energy (a.u.)			
	STO-3G	4-31G	A^*	STO-3G	4-31G	A^*	B^{**}
$1a_1$	-25.9442	-26.2151	-26.2774	-19.5131	-20.0891	-20.1891	-20.1662
$2a_1$	-11.1077	-11.2957	-11.3240	-10.7124	-10.9810	-11.0325	-11.0228
$3a_1$	- 1.4880	- 1.5743	- 1.5910	- 0.7466	- 0.9288	- 0.9777	- 0.9458
$4a_1$	- 0.8958	- 0.9526	- 0.9595	- 0.4897	- 0.6060	- 0.6335	- 0.6268
1e	- 0.5912	- 0.6861	- 0.6968	- 0.2353	- 0.3331	- 0.3592	- 0.3233
$5a_1$	- 0.5512	- 0.6511	- 0.6639	+ 0.0049	- 0.1920	- 0.2379	- 0.2398
2e	- 0.4213	- 0.5230	- 0.5323	+ 0.1864	- 0.0504	- 0.0947	- 0.0824

Total energy (a.u.)			Total energy (a.u.)			
STO-3G	4-31G	A^*	STO-3G	4-31G	A^*	B^{**}
-137.163	-138.857	-139.035	-112.690	-114.211	-114.393	-114.417

A^* ; [5s3p/3s] + diffuse B^{**} ; Double zeta + polarization (S.Ikuta. unpublished)

The orbital and total energy in the ground state parent and daughter calculated with the above basis set are given in Table 1. For the comparison, the calculated results with STO-3G[10] and 4-31G[11] basis sets are also listed. The electron configurations of the parent and the daughter in the ground state are both $(1a_1)^2(2a_1)^2(3a_1)^2(4a_1)^2(1e)^4(5a_1)^2(2e)^4$. In CH_3O^-, the results with STO-3G basis set are fairly different to those with the extended basis set, and especially the orbital energy in $5a_1$ and 2e is quite different. Therefore, it is obvious that the extended basis set is indispensable to the calculation for an negative ion.

Table 2. Transition probability (P_{gm}) of the $CH_3{}^{18}F$ β^+-decay.

Final state (m)	$\Delta E_m{}^*$	P_{gm}
Ground state	0	0.6709
$2e \longrightarrow 6e$	8.35	0.0269
$2e \longrightarrow 7e$	10.45	0.0396
$5a_1 \longrightarrow 17a_1$	20.02	0.0102
$2e \longrightarrow 10e$	30.20	0.0572
$5a_1 \longrightarrow 20a_1$	36.12	0.0111

$\Delta E_m{}^*$; The energy relative to the SCF energy (eV).

The calculated results with the extended basis set are very similar to those already reported by Yarkony et al.[12] The wavefunctions obtained with [5s3p/3s] + diffuse functions were used for the calculation of the transition probability.

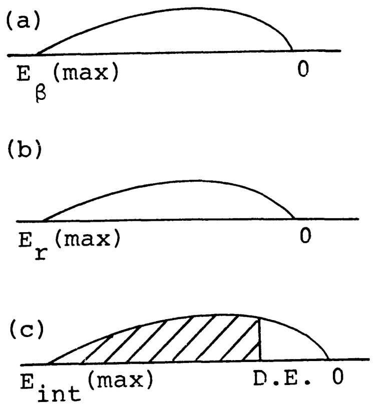
In Table 2 are listed the transition probability from the parent to the daughter in the ground and some excited states. The final states listed are those with substantial probability and those with the excitation energy lower than 40 eV.

After the β^+-decay, 67 % of $CH_3{}^{18}F$ goes to the CH_3O^- in the ground state, and sum of the transition probability to some low-lying excited states of the daughter is not negligible.

The CH_3O^- in the ground state is calculated to be bound against $C\text{-}O^-$ and C-H bonds.[13]

The first ionization potential of CH_3O^-, as shown in Table 1, is expected to be 2.57 eV on the basis of the Koopman's theorem. Then, the final excited states listed in Table 2 must be well in the continum, and the electrons will be easily ejected. Therefore, the probability of the electron shake-off process in $CH_3{}^{18}F$ will be about 30 %, which is the sum of the transition probability to the excited state daughters. This probability on electron shake-off is almost the same as that in ^{18}F atom (27.9 %) calculated by Carlson and White.[2)]

There exists a distribution of energy in the β^+-ray emitted from ^{18}F. Therefore, the recoil energy and the internal energy per chemical bond given by β^+-ray also have a distribution as shown in Fig. 1. The maximum recoil energy and maximum internal energy per chemical bond by 0.65 MeV β^+-ray can be estimated to be 31.3 and 3.5 eV, respectively, using the well-known equations.[14)] Since this maximum internal energy was obtained in the supposition that the internal energy is equally distributed among four chemical bonds, it seems that real maximum internal energy on $C-O^-$ bond will be larger than 3.5 eV. Therefore, the $C-O^-$ bond will be broken in the region (denoted the oblique line in Fig. 1-c) that the internal energy is greater than the bond dissociation energy. Relatively large amounts of CH_3O^- formed following the β^+-decay will be easily broken by the recoil effect of β^+-ray.



E_β(max); maximum energy of β^+-ray.
E_r(max); maximum energy of recoil energy.
E_{int}(max); maximum internal energy on $C-O^-$ bond.
D.E.; dissociation energy of $C-O^-$ bond.

Fig.1. Energy distribution of β^+-ray (a), recoil energy(b), and internal energy on $C-O^-$ bond(c).

The yield of CH_3O^- obtained by Carlson and White[2)] is only 12 % and the total yield of the positive ions (CH_3^+, CH_2^+, CH^+, C^+, and H^+) amounts to 63 %. The low value on CH_3O^- does not conflict to the above considerations on the recoil effect. Some fraction of the yield of positive ion species may be derived from the decomposition of CH_3O^+ produced through the electron shake-off process. However, other species cannot be fully interpreted without the considerations about the collection efficiency of the positive and negative ions and the theoretical study of the dynamics of the recoil event.

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