An *ab initio* Investigation into the $S_N2$ Reaction: Frontside Attack versus Backside Attack in the Reaction of $F^-$ with $CH_3F$

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The energy hypersurface for the attack of fluoride ion on methyl fluoride has been explored with *ab initio* LCAO-SCF calculations at a split-valence basis set level. Transition states for frontside and backside attack have been located. In addition to transition states, two possible $F^-\cdot CH_3F$ clusters have been identified. The transition state for the substitution of fluoride with retention of configuration is found to be 56 kcal/mol higher than the transition state for inversion of configuration. The transition state for hydride displacement with inversion is 62 kcal/mol above the transition state for fluoride substitution with inversion.

**Key words:** $S_N2$ reaction, frontside versus backside attack - $CH_3F_2^-$ - Geometry optimization, force method

1. Introduction

The bimolecular nucleophilic substitution ($S_N2$) reaction is central to organic chemistry, and its energetics and stereochemistry have been the subject of extensive experimental investigations\(^1\). Without known exception, the $S_N2$ reaction at carbon centers proceeds with inversion of configuration.

With advances in computational capabilities, theoretical examinations of the $S_N2$ reaction have become increasingly feasible\(^2\). For a number of representative examples, high quality *ab initio* calculations already exist [2-14]. *A priori*, a theoretical investigation should consider all possible directions of attack by the nucleophile. These paths can be broadly divided into the two categories of frontside and backside attack. For the latter, the path of the approaching nucleophile lies within the trigonal pyramid formed by the central atom and the three non-participating substituents; this trajectory invariably leads to the familiar Walden inversion\(^1\). On the other hand, frontside traject-

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\(^1\) For an authoritative account, see Ingold [1].

\(^2\) A review of theoretical investigations of the $S_N2$ reaction has recently been provided by Bader and Gangi [2].
tories can, at least in principle, lead to displacement with retention. Since this stereochemical course is never observed for $S_N2$ displacements at carbon, the cost in energy for this approach is presumably relatively high.

The simplest theoretical model for the $S_N2$ reaction, $\text{CH}_4 + H^-$, has received the most attention [3-5, 8, 9, 12-14]. Details of the minimum energy pathway involving backside attack are well documented [5, 8, 9], and most theoretical investigations on larger systems, such as $\text{CH}_3X + Y^-$ ($X, Y = F, Cl, CN$) [6-13] and $\text{NH}_3\text{F}_2$ [41], have also been restricted to backside attack. Aside from certain semi-empirical studies [15-17], comparatively little is known about frontside attack for systems other than $\text{CH}_3^-$ [3, 4, 38]. To fill this gap in our understanding of the $S_N2$ reaction, we have investigated in some detail the energetics of frontside attack for a chemically more realistic system, $\text{CH}_3\text{F} + F^-$. 

2. Calculations

The SCF wave functions used in the present work were calculated using the standard GAUSSIAN 70 program package [18] with the STO-3G and 4-31G basis sets [19, 20]. Computations were performed on the CDC Cyber 76 at Bologna (single precision arithmetic, 60-bit word) and on the IBM 360/91 at Princeton (double precision, 32-bit word).

A preliminary survey of the energy hypersurface of $\text{CH}_3\text{F} + F^-$ indicated that the STO-3G basis set was unsuitable for our purposes. As shown in the Appendix, and in contrast with better ab initio calculations [8] which predict the existence of a transition state for the $S_N2$ reaction with backside attack, calculations with the STO-3G basis set predict a stable intermediate. This suggests that estimates of geometries and energy differences obtained at the minimal basis set level can be grossly misleading. The 4-31G basis set, on the other hand, is capable of reproducing a (local) transition state (see below).

The geometry optimizations and energy calculations reported in the body of this paper were performed with the 4-31G basis set. It should be noted that this basis set is of double zeta quality in the valence region but does not contain angular polarization functions (i.e., $p$ orbitals on H, $d$ orbitals on C and F). The 4-31G basis set for fluorine is known to be poorer in quality than the carbon basis set [20]. Furthermore, it should be pointed out that anionic systems are notoriously difficult to represent accurately with small or moderate size basis sets [21]. Despite these known shortcomings, the 4-31G basis set was used in the present work. Since the location of intermediates and transition states requires an extensive search of geometries, computations with a larger, more accurate basis set were beyond our reach for economic reasons.

Some preliminary geometry optimization was performed with the built-in facilities of GAUSSIAN 70. Convergence to the final geometries was achieved with the force method [22, 23]. In this technique, the forces on the atoms in a molecule are calculated analytically (a process roughly as expensive as the calculation of the electronic energy of the molecule). Then these forces, along with force constants obtained either...