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Unusual reaction paths of S_N2 nucleophile substitution reactions $CH_4 + H^- \rightarrow CH_4 + H^-$ and $CH_4 + F^- \rightarrow CH_3F + H^-$: Quantum chemical calculations

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ABSTRACT

Quantum chemical (CCSD(full)/6-311++G(3df,3pd), CCSD(T)(full)/6-311++G(3df,3pd)) and density function theory (B3LYP/6-311++G(3df,3pd)) calculations were performed for the S_N2 nucleophile substitution reactions $CH_4 + H^- \rightarrow CH_4 + H^-$ and $CH_4 + F^- \rightarrow CH_3F + H^-$. The calculated gradient reaction pathways for both reactions have an unusual behavior. An unusual stationary point of index 2 lies on the gradient reaction path. Using Newton trajectories for the reaction path, we can detect VRI point at which the reaction path branches.

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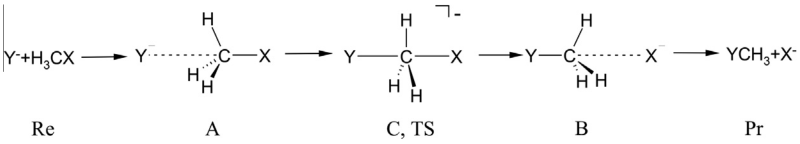
1. Introduction

Mechanisms of a gas-phase bimolecular nucleophilic substitution at the tetrahedral carbon atom [1] are ones of those which are well studied experimentally [2–6] and theoretically [1,7–18] however their reaction pathways on the corresponding potential energy surface (PES) may be quite complex [15,17] and they remain not enough studied.



The paths of such reactions begin with the formation of the pre-reaction complex (intermediate) **A** of reagents (**Re**) which usually corresponds to a minimum on the potential energy surface (PES) of the system. Then pathways pass through the transition state **C** corresponding to the saddle point on the PES, and terminate at the minimum corresponding to the second pre-reaction (intermediate) complex **B** of products (**Pr**). The energy profile of this reaction has a simple double-well form, separated by an energy barrier. The pathway of a reaction, according to various calculations, is observed for almost all studied nucleophiles X, Y [1–18]. Although the distribution of stationary points (SPs) (minima and saddle points) on the PES in the reaction zone can be quite complicate [15,17].

It was shown earlier [19] that the chemical system can infinitesimally slowly slide down on the PES along gradient lines (steepest descent lines), which, like equipotential lines, cannot branch outside of stationary points. Such a path goes downhill in both directions of the transition vector at the saddle point on the PES and enters the adjacent stationary points. It is called gradient reaction path [19]. The gradient reaction pathway is similar to the IRC [20] in the case of Cartesian coordinates with mass weighting. It is well adapted to the topology of the PES, which is observed for almost all the studied gas phase S_N2 reactions [1–18]. However, when the PES topology has a more complex structure, gradient lines are not fine enough [21–25].

In this paper we discuss a case where nucleophiles X, Y are the hydride anions X, Y = H, or hydride and fluoride anions $X = H^-$, $Y = F^-$. The IRC path which is supposed as a smooth continuous line,

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connects the saddle point of index one, **C**, (the transition state) downhill with a SP of index 2, point **B**, which corresponds to the top of a two-dimensional hill, cf. Ref. [21]. Such combination has to be characterized by a VRI (valley-ridge inflection) point [25–36] in between. There are infinitely many gradient lines from point **B** to every neighboring minimum. The detection of the VRI point can be realized by the use of Newton trajectories (NT). The curves bifurcate at VRI points. However, gradient lines do not bifurcate outside stationary points.

It has been shown by Wales [37] and by Quapp [38] that the VRI point is coordinate invariant. (However, it is not invariant on the quantum chemical method to calculate the PES.) If it exists it is on the PES in any coordinate system and characterizes the PES topology. From the saddle point **C** (transition state of index one) on the PES to the tangential direction of the transition vector only one gradient line leaves and this gradient line terminates at the stationary point **B**. This follows from symmetry arguments. Only a bifurcating NT can open the insight into the possibilities of bifurcating reaction pathways which circumvent hilltop **B**. After point **B**, the flow of infinitely many gradient lines goes down to the product minimum. So we have the queer case in that the IRC from the transition state to the product minimum does not consist of only one continuous line but of infinitely many lines.

2. Methods

All calculations to find the stationary points in this paper were performed by standard methods of coupled cluster CCSD, CCSD(T) methods including all electrons (keyword "full") and the density functional theory method B3LYP in the triple-split basis set 6-311++G(3df,3pd) using the Gaussian 03 software package [39]. Optimization of molecular geometry in stationary points at all levels of approximation has been performed with the convergence criteria "tight". No counterpoise corrections were made for the basis set superposition error (BSSE) [40–43] in calculations. All results refer to the gas phase. The calculations of NTs where coupled with the GamessUS package [44–46] where the B3LYP/6-311G(df,pd) method is used.

We calculate NTs by an Euler-Branin-step method following along the direction of the vector field **A g** of the so called Branin differential equation [47]

$$d\mathbf{x}/dt = + - \mathbf{A}(\mathbf{x})\mathbf{g}(\mathbf{x}),$$

where **A** is the adjoint matrix of the Hessian, and **g** is the gradient of the surface, and *t* is a curve length parameter. The iteration of the exact value of the VRI coordinates is done by the two methods described in Refs. [34,35]. The methods allow us to exactly get the singular NT which meets the VRI point and branches there.

3. Results and discussion

3.1. Stationary points on the CH_5^- and FCH_4^- PES's

The performed quantum chemical calculations show that the PESs of the CH_5^- and FCH_4^- S_N2 reactions (1) have stationary points in the region of the structures **1–9**. The geometric characteristics of these structures are shown in Figs. 1 and 2. Total and relative values of the energy, as well as of the values of the zero point energy in the harmonic approximation (ZPE) for the structures of **1–9** and isolated molecules of methane, fluorometane, hydride and fluoride anions are given in Table 1. Structures corresponding to the radicals or results of a system decay are not considered. According to the calculations, the structure of **1**, **5** and **9** corresponds to the minimums ($\lambda = 0$), the **2**, **4**, **6** and **8** are saddle points of index one ($\lambda = 1$), and the structures **3** and **7** correspond to the top of the "two-dimensional hill" ($\lambda = 2$), thus they are saddle points of index two.

It is important to note that the results obtained by different methods are in mutual agreement with each other and with the data of earlier studies [48,49]. The calculated geometry of methane CH_4 and fluoromethane FCH_3 are also in mutual agreement with MW measurements [50].

3.2. Reaction $CH_4 + H^- \rightarrow CH_4 + H^-$

According to calculations, the S_N2 reaction $CH_4 + H^- \rightarrow CH_4 + H^-$ begins with the formation of the di-hydrogen bonding complex **1**, having an energy formation ~2 kcal mol^{-1} (see Scheme 1 and Table 2). The length of the H...H bond and the energy formation (see Table 2) in complex **1** is comparable to a similar length and energy in other complexes with H...H bonding [51]. Note that the inclusion of ZPE does not greatly reduce the complex formation energy.

On the CH_5^- PES there are three equivalent minima of **1′**, **1″**, **1‴** with a different orientation of the $H\cdots H_{1,2,3}C$ bonding. These three minima are separated by three transition states **2′**, **2″**, and **2‴**

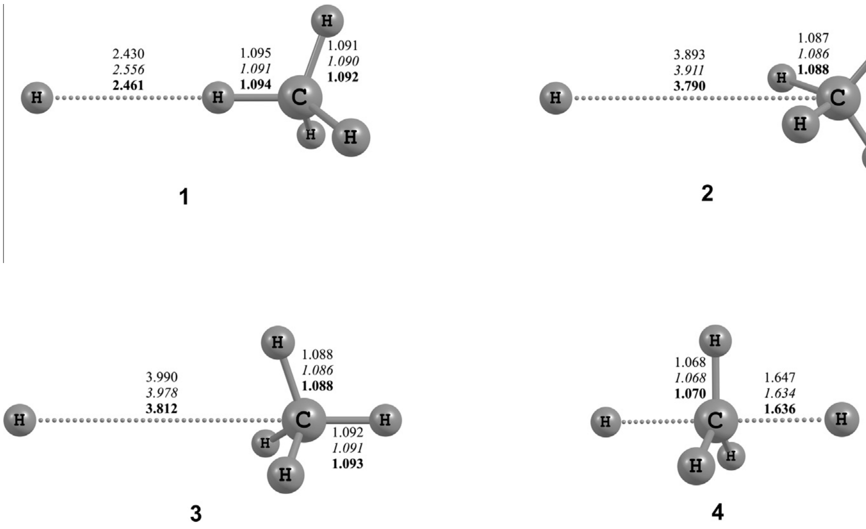

Fig. 1. Geometrical parameters for structures **1–4** are predicted by B3LYP/6-311++G(3df,3pd) (plain), CCSD(full)/6-311++G(3df,3pd) (italic) and CCSDT(full)/6-311++G(3df,3pd) (bold) methods. Bond lengths are given in Å.

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