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Analysis of Vibration Mode for $H_2+F\rightarrow HF+H$ Reaction Mechanism: Density functional Theory Calculation

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Abstract: Three density functional theory methods (DFT) have been used to investigate the $H_2+F\rightarrow HF+H$ reaction comparing with the Hartree-Fock method and Moller-Plesset (MP2) perturbation theory method. Through the analysis of the vibrational mode and vibrational frequency in the reaction process, the reaction mechanism has been discussed. The activation energy, the reorganization energy and rate constant of the ET reaction are calculated at semi-quantitative level.

Keywords: Density function theory, vibratonal mode, vibrational frequency.

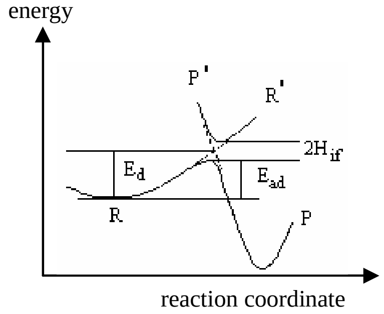
As one of the simplest chemical reactions $A+BC\rightarrow AB+C$, the prototypical reaction, $F+H_2\rightarrow HF+H$, along with its isotopic variants, has been one of the most thoroughly investigated reactions in chemical reaction dynamics both in experimental and theoretical fields. For the $A+BC\rightarrow AB+C$ reaction, in the process of the A atom of initial state incoming towards the reaction region, provided that the interaction between A and BC is strong, according to the Franck-Condon principle, the internuclear distance of the molecule BC will be unchangeable just after the electron is transferred because of the much faster velocity of the moving electron; while when the interaction between the reactants is so small that with the distance of A and BC reducing, the bond of BC lengthens. In this process, the reaction does not give out (or absorb) any heat. These are the non-adiabatic and adiabatic process, respectively. For this $F+H_2\rightarrow HF+H$ instance, which can be expressed by the **Figure 1**.

In this figure, E_d denotes the non-adiabatic activation energy corresponding to the energy difference between the crossing point and the reactant's minimum point under the assumption that the reacting system experiences a non-adiabatic electron transfer process; E_{ad} denotes the adiabatic activation energy. The coupling matrix element, H_{if} , representing the interaction between acceptor and donor, can be expressed by[1]:

$$H_{if} = E_d - E_{ad} \qquad (1)$$

For this reaction, it has been studied from various aspects[2]. In this article, we will mostly discuss the vibration mode and vibration frequency in the reaction process and

Figure 1 Energy profiles of non-adiabatic states and the adiabatic states



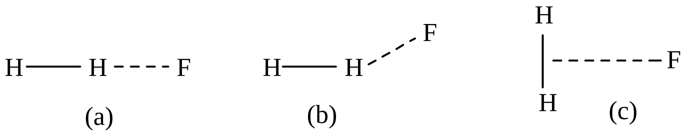
for this reaction, it has been studied from various aspects[2]. In this article, we will mostly discuss the vibration mode and vibration frequency in the reaction process and through the calculation of some parameters, the rate constant will be derived. In the present paper, three DFT methods-BLYP, B3LYP and B3P86 have been used to investigate the process of reaction (1) comparing with the Hartree-Fock method and the second order of Moller-Plesset (MP2) perturbation theory method at 6-311g** basis set for higher accuracy. All calculations are carried out using the Gaussian- 94 package.

Results and Discussion

The equilibrium geometry of the complexes in precursor complex

For the precursor complex, three possible structures have been considered upon contact between the reactants (shown in **Figure 2**):

Figure 2 The sketch of three molecular structures for the precursor complex



Geometry optimizations were performed for structures of (a), (b) and (c) using various methods. In the process of optimizing the three geometries, the FHH angle of (b) becomes close to 180°, that is to say, it is similar to (a); for (c), the result showed no stable position with the distance of the center of H_2 molecule and the F atom decreasing, while (a) has a stable state. Our further discussion will be restrict to structure (a). In calculations, we use a cycle which mainly including a process of two steps to optimize the precursor complex: (1) keeping the optimized geometry of the molecule H_2, the distance R between F atom and the adjacent H atom is optimized; (2) fixing the optimized R, the distance r between the two H is optimized, then the r derived from (2) is used to repeat the step (1), the cycle is performed at all times until the variables of r and R do not change, thus the geometry of the precursor complex can be defined by two parameters R and r (the FHH angle is fixed to 180 degree).

The analysis of the vibrational mode and vibrational frequency in the reaction process

To understand the reaction mechanism of this reaction further, we analyzed the vibrational mode and vibrational frequency in the process, which are listed in the **Table 1**.

Table 1 Vibrational mode and vibrational frequency for various species in the reaction process

Species	Sym	UHF	UMP2	UBLYP	UB3LYP	UB3P86	Assignment
reactant	SG	4592.4	4533.2	4345.2	4419.4	4420.5	H-H s. str.
precursor	SG	15.35	40.18	13.84	16.68	17.00	H-F s. str.
complex	PI	34.00	5.90	21.96	13.05	13.50	H-H bending
	PI	34.00	5.90	21.96	13.05	13.50	H-H bending
	SG	4594.1	4535.6	4344.7	4418.2	4418.2	H-H s. str.
transition	SG	i2924.3	i1232.6	i8.00	i36.14	i79.12	H-F s. str.
state	PI	621.7	140.7	i80.32	73.83	i382.1	H-H bending
	PI	621.7	140.7	i80.32	73.83	i382.1	H-H bending
	SG	1915.1	3316.	4335.3	4418.9	4405	H-H as. str.
successor	SG	37.68	71.04	220.2	206.3	232.5	H-H s. str.
complex	PI	39.14	94.22	212.9	194.4	218.5	H-F bending
	PI	39.14	94.22	212.9	194.4	218.5	H-F bending
	SG	4491.2	4194.1	3813.6	4016.0	4026.5	H-F s. str.
product	SG	4491.2	4195.6	3940.8	4099.2	4140.4	H-F s. str.

From **Table 1**, it can be seen that the reactant, linear molecule hydrogen, has a symmetrical stretching vibrational mode. For the precursor complex, it is obvious that the vibrational modes increase to four which including a mode of H-H symmetrical stretching, two modes of H-H bending and a mode of H-F symmetrical stretching, this is due to the effect of the F atom attacking on the hydrogen molecule. However, the influence of the vibrational mode on the precursor is small, which can be seen from the little values of the vibrational frequency of the H-H bending and the H-F symmetrical stretching. By comparing the vibrational modes and vibrational frequencies of transition state with those of the precursor complex, it can be found that the H-F symmetrical stretching has an imaginary frequency, this indicates that the transition state possesses a higher energy level and it is unstable. Contrasting the numerical values of the vibrational frequency, it can be seen that the worst agreement between the calculated and other results is found in UHF/6-311g** results. There is a large overestimation of the frequencies at UHF level, maybe this is due to the underestimated bond lengths and a result of neglecting electron correlation in the HF theory. Even when scale factors were considered, the results are still worse than DFT methods. This result is in agreement with those of our recent paper[3, 4]. Comparing to the BLYP, B3LYP and B3P86, the MP2 method has also biggish error. It can be also seen that the vibrational frequencies of H-F symmetrical stretching for the transitional state changed largely, that is due to the curvature in the transition state is very different, while the change of the H-H vibrational frequency is not large. When the transition state transforms to successor complex gradually, the H-F symmetrical stretching vibrational frequency changes from an imaginary value to the highest value, which indicates the formation of the H-F bond. When the successor complex transforms to the product, the H-H bond is ruptured and the vibrational mode is changed once again, *viz.* the H-F symmetrical stretching vibration.

On the basis of the harmonic oscillator model, the George-Griffith-Marcus method puts forward an expression for the inner-sphere reorganization energy：

$$\lambda = 2n[f_z f_{z+1}/(f_z + f_{z+1})](\Delta q)^2 \qquad (2)$$

where the subscripts z and z+1 denote the charge numbers of the reduced and oxidized species respectively, n is the number of ligand or solvent molecules in the inner-sphere, f_z and f_{z+1} are the force constants of the ion-ligand bonds in the reduced and oxidized species, respectively, and $\Delta q=q_z-q_{z+1}$ is the equilibrium bond length difference between the reduced and the oxidized species. According to the classical oscillator model, the force constant *f* can be expressed by:

$$f = 4\pi^2 c^2 \omega^2 \mu / N \qquad (3)$$

where ω is the stretching vibration frequency, μ is the reduced masses, and N is the Avogadro constant. We have calculated the force constants of the various stages for the reaction, then the reorganization energy λ can be calculated. On the basis of the optimization, the adiabatic activation energy E_{ad} has been obtained; the non-adiabatic activation energy E_d can also be computed by fitting the calculated energy points to an three-degree polynomial in r (which correlation coefficient is 0.997), so the H_{if} will be derived; according to the Eq.(1), and the rate constant k will also be calculated. These results are listed in **Table 2**.

Table 2 Three parameters and the rate constant for the reaction system:

Items	H_{if} (cm^{-1})	λ (kj/mol)	$\Delta G^{\#}$ (kj/mol)	k(s^{-1})
Data	227.5	4.19	13.44	2.82×10^{11}

In conclusion, the vibrational mode and vibrational frequency in the reaction of $H_2 + F \rightarrow HF + H$ have been studied in this paper. First, the geometry optimization of the precursor complex was performed and the results showed that there was a linear structure for this state. Subsequently, various methods have been used to optimize the precursor complex, the transitional complex and the successor complex, and by analyzing the vibrational mode and vibrational frequency, the reaction mechanism was confirmed. Finally, the rate constant was obtained at semi-quantitative level.

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