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Dynamics of the Termolecular (HF + HF + HF) Reaction

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ABSTRACT The termolecular interaction among three hydrogen fluoride molecules has been modeled as taking place between a hydrogen fluoride dimer $(HF)_2$ and a hydrogen fluoride molecule. An accurate multi-dimensional potential energy surface (PES) that can fully describe the interaction among the three reacting molecules is still not available. We have overcome this problem by calculating the PES of this system using the London-Eyring-Polanyi-Sato (LEPS) formulation. The energy barriers and well depths are in good agreement with *ab initio* calculations. We have adopted the quasi-classical trajectory (QCT) method to simulate the dynamics of the six-centered hydrogen bond exchange reaction. In this paper we present our formulation of the QCT approach to simulate this reaction in which over 100,000 trajectories have been computed. Opacity functions and reaction cross section for reactive trajectories are reported. We find that the six-centered bond exchange reaction between the three HF molecules do take place but with low probability. Assisted six-centered reactions and monomer exchange reactions also take place to a greater extent. Vibrational excitation of reactants also play an important role in the enhancement of reactivity.

ABSTRAK Interaksi termolekul antara tiga molekul hidrogen fluorida telah dimodelkan sebagai interaksi antara dimer hidrogen fluorida $(HF)_2$ dan satu molekul hidrogen fluorida. Permukaan tenaga keupayaan banyak dimensi yang tepat, yang boleh menjelaskan sepenuhnya interaksi antara tiga molekul masih belum wujud. Oleh kerana itu, kami telah menggunakan formulasi London-Eyring-Polanyi-Sato (LEPS) untuk mengira permukaan tenaga keupayaan untuk sistem ini. Nilai rintangan tenaga dan kedalaman perigi tenaga yang dikira bersetuju dengan nilai yang diperolehi dari pengiraan *ab initio*. Kami telah menggunakan kaedah trajektori kuasi klasikal (QCT) dalam menyelakukan dinamika tindakbalas pertukaran ikatan hidrogen enam pusat ini. Didalam kertas kerja ini, kami mempersembahkan formulasi QCT dalam menyelakukan dinamika sistem ini. Lebih dari 100,000 trajektori telah dikaji. Fungsi opasiti dan keratan rentas tindakbalas untuk trajektori yang reaktif dilaporkan. Kami mendapati bahawa tindakbalas pertukaran ikatan enam pusat antara tiga molekul HF berlaku hanya dengan kebarangkalian yang kecil. Tindakbalas enam pusat berbantu dan pertukaran monomer juga berlaku dengan kebarangkalian yang lebih tinggi. Pengujaan getaran bahan tindakbalas juga memainkan peranan yang penting dalam mempertingkatkan kereaktifan.

(Termolecular reaction, potential energy surface, six-centered reaction, quasi-classical trajectory)

INTRODUCTION

A reaction that involves the participation of three molecules in an elementary step is a termolecular reaction. It is a well known fact that termolecular reactions are rare due to the low probability of three molecules coming together simultaneously with appropriate energy and in the right orientation to form the transition state leading to the products. Hence very few termolecular reactions are reported in the literature compared to bimolecular or unimolecular reactions. Termolecular reactions also receive less attention due to the difficulty to study such reactions experimentally and also in the simulation of these reactions by computational methods. Well known examples of termolecular reactions are atomic recombination reactions and oxidation of nitric oxide (NO). These reactions are important in combustion and atmospheric chemistry. A model six-centered (6C) hydrogen exchange reaction between three hydrogen molecules has been studied by quasi-classical trajectory (QCT) method [1, 2]. A similar 6C reaction

$$(HI)_2 + F_2 \rightarrow HF + HI + IF$$

has been reported by Durana and McDonald [3].

Both collision theory and transition state theory have been used to explain termolecular reactions. The application of collision theory to three-body collisions involving atoms is found to give more satisfactory treatment of termolecular reactions [4]. Two mechanisms [5, 6] for termolecular reactions have been proposed a) direct three-body collision and b) sequential two-body collisions involving the formation of a bound complex or dimer. As a part of our efforts to understand termolecular reactions, we are investigating the hydrogen atom exchange between three hydrogen fluoride molecules that involves hydrogen bonding.

Hydrogen fluoride serves as a prototype in the study of hydrogen bond dynamics. There are numerous *ab initio* investigations [7 - 9] of the $(HF)_3$ trimer that provide information on the equilibrium geometry, energetics and vibrational frequencies of the HF trimer. The *ab initio* studies have shown that the equilibrium geometry has a cyclic structure with a C_{3h} symmetry and this structure has been confirmed experimentally [10, 11]. The energetics of this system has also been studied using different levels of *ab initio* theory and basis sets. Klopper *et a*l. [12] have made a summary of these results.

The interaction of three HF molecules has some interesting features. It is the simplest cyclic system that exhibits hydrogen bonding. There are two competing processes i.e. six-centered (6C) vs. four-centered (4C) processes. The 6C reaction is symmetry-allowed based on Woodward-Hoffmann rule [13]. Of prime importance in a dynamical study of chemical interactions is the availability of a global potential energy surface of the system that is under investigation. An analytical form of the potential energy function of this system is still not available and quantum-mechanical calculations of the potential energy of a system with six atoms, thirty electrons in a twelve dimensional hypersurface is a difficult task. Most of the accurate (*ab initio*) calculations have been done for triatomic systems. We have calculated the PES based on the LEPS formulation [14]. It should be emphasized that the difficulty of getting a good PES of this six-atom system is due not only to the high dimensionality of the surface but also due to competing 6C and 4C processes. These processes impose additional constraints in getting acceptable energy barriers and well-depths such that the energy barrier for the 6C reaction is less than the 4C reaction. We have used the quasi-classical trajectory (QCT) method to simulate the dynamics of the interactions between the three HF molecules. We hope to achieve the following: a) Determine the reactivity of the reactive product channels (reaction probability, opacity functions and reaction cross sections), b) Determine the role of reagent energy in promoting reaction, c) Determination of energy product distribution and d) Determine mechanisms by which these processes occur. Work is still ongoing so currently we will be able to answer only some of these questions.

METHODS

Details of the QCT method has been described elsewhere [15]. We discuss only some key points of the method as it applies to the $(HF)_3$ system. The motion of the atoms can be described by Hamilton's equations of motion

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \qquad \dot{p}_i = \frac{\partial H}{\partial q_i}(i = 1,2 \ldots 3N) \qquad (1)$$

where q's are the Cartesian co-ordinates and p's are the conjugate momenta of an N-particle system. H is the classical Hamilton of the system defined by $H = T + V$ where T is the kinetic energy and V is the potential energy (PE) of the system. For systems with more than three atoms, the Cartesian coordinates is most suitable [16]. Three co-ordinate systems used in this study are: (i) Molecule-fixed co-ordinates with the center-of-mass (CM) of the respective HF molecules as the origin. (ii) Molecule-fixed co-ordinates for the VDW molecule $(HF)_2$ with the CM of the VDW molecule chosen as the origin. (iii) Spaced-fixed co-ordinates XYZ, with CM of the whole system (hexa-atomic) as the origin. Using the Cartesian coordinates, the kinetic energy and potential energy are given by,

$$T = \frac{1}{2}\sum_{i=1}^{18}\frac{p_i^2}{m_i} \quad \text{and} \quad V = V(q_1, q_2, \ldots q_{18}) \qquad (2)$$

The equations of motion are:

$$\dot{q}_i = \frac{p_i}{m_i} \quad \text{and} \quad \dot{p}_i = -\frac{\partial V}{\partial q_i} (i = 1,2...18) \qquad (3)$$

Hence, to solve these equations, we need to know derivatives of potential energy with respect to coordinates, in addition to the initial conditions (coordinates and momenta).

Potential Energy Surface

As a prerequisite to the dynamics study we first calculate the PES for the $(HF)_3$ using the approach of London, Eyring and coworkers [18, 19]. Thompson and Suzukawa [17] have used this approach to study 6C reactions. We have followed the same approach to calculate the potential energy of the $(HF)_3$ system using the parameters given in Table 1. The PES of the $(HF)_3$ system shows the presence of two potential wells indicating the stability of the $(HF)_3$. The saddle point on the PES locates the transition state structure (D_{3h} symmetry). Table 2 gives a comparison of our work with those from *ab initio* studies. Despite the four constraints in the energy barrier and well-depth for the 4C and 6C processes, we are able to obtain a surface which is comparable to the best *ab initio* values. A plot of the potential energy surface of the $(HF)_3$ system using LEPS formulation is shown in Figure 1.

The termolecular collision between the three hydrogen fluoride molecules is modeled between an HF dimer and another hydrogen fluoride molecule. We have calculated the interaction energy of the HF dimer from our model PES by subtracting the monomer energies and by keeping one monomer at a large distance (>10 Å). The internuclear distance between the two monomers of the dimer is selected from a Morse potential. The coordinates of all six atoms in the space-fixed frame is obtained after applying the appropriate transformations of the molecule-fixed coordinate (Figure 2).

Selection of Initial Conditions

In the present calculations, we have restricted ourselves to the fixed values of vibrational quantum number (v_i), rotational quantum number (J_i,), impact parameter (b), and relative velocity (V). Once the initial conditions are selected, the corresponding coordinates and momenta calculated, the equations of motion are solved numerically. A step size of Δt = (0.2 - 0.4) x 10^{-16} s was used. The accuracy of the integration was checked by the energy and angular momentum conservation and back integration.

Table 1. Potential Energy Parameters for H_2,F_2 and HF

PARAMETER	H_2[20]	F_2[21]	HF[20]
^1D(kcal/mol)	109.4592	38.2796	141.0516
r_e(Å)	0.7419	1.4180	0.9171
α(Å^{-1})	1.9735	2.9019	2.2204
^3D(kcal/mol)	45.3555	46.6838	86.1300
β(Å^{-1})	1.8900	3.9499	2.4255

Table 2. Energy barrier and well-depth for the 4C and 6C processes [22]

METHOD	EB(6C)	EB(4C)	EW(6C)	EW(4C)
LEPS (this work)	5.5	43	-15	-6.1
Best *ab initio*[a]	5.0	42	-13	-5.0

Product Channels

All possible product channels resulting from the collision between the dimer $(HF)_2$ and the other HF molecule are as shown in Table 3. To distinguish different chemical species, small letters a, b and c are used whereas the numbering of atoms is used for computational purposes. We have identified 18 different product channels for the interaction of the three HF molecules. These product channels are summarized into 5 different types of 'chemical reactions' as shown in Figure 3. R1 represents non-reactive process whereby the HF dimer remains intact. R2 involves the dissociation of starting dimer. R1 and R2 are grouped together because the two channels do not involve any exchange of bonds or monomers.

R3 is a genuine 6C reaction that involves hydrogen bond exchange reaction where the combination of atoms results in formation of three 'new' HF molecules. Figure 4 shows one of the two possible channels for a genuine 6C process. Reactions R4, R6, R8 and R10 produce HF, H_2 and F_2. There are 6 channels that can form these products via 6C process but we do not expect these reactions to take place due to higher energy requirements. In R5, R7 and R9, the third HF molecule transfers its energy to the dimer molecule leading to bond exchange among the atoms in the dimer. For R11, exchange of monomer takes place resulting in the formation of a new dimer. To identify which processes have occurred, we make use of the distance criteria. All the 15 internuclear distances are compared and the integration continued until only three of the distances are less than a specific distance R_s (set at 8.5 Å) after which the integration is stopped and the products identified and analyzed.

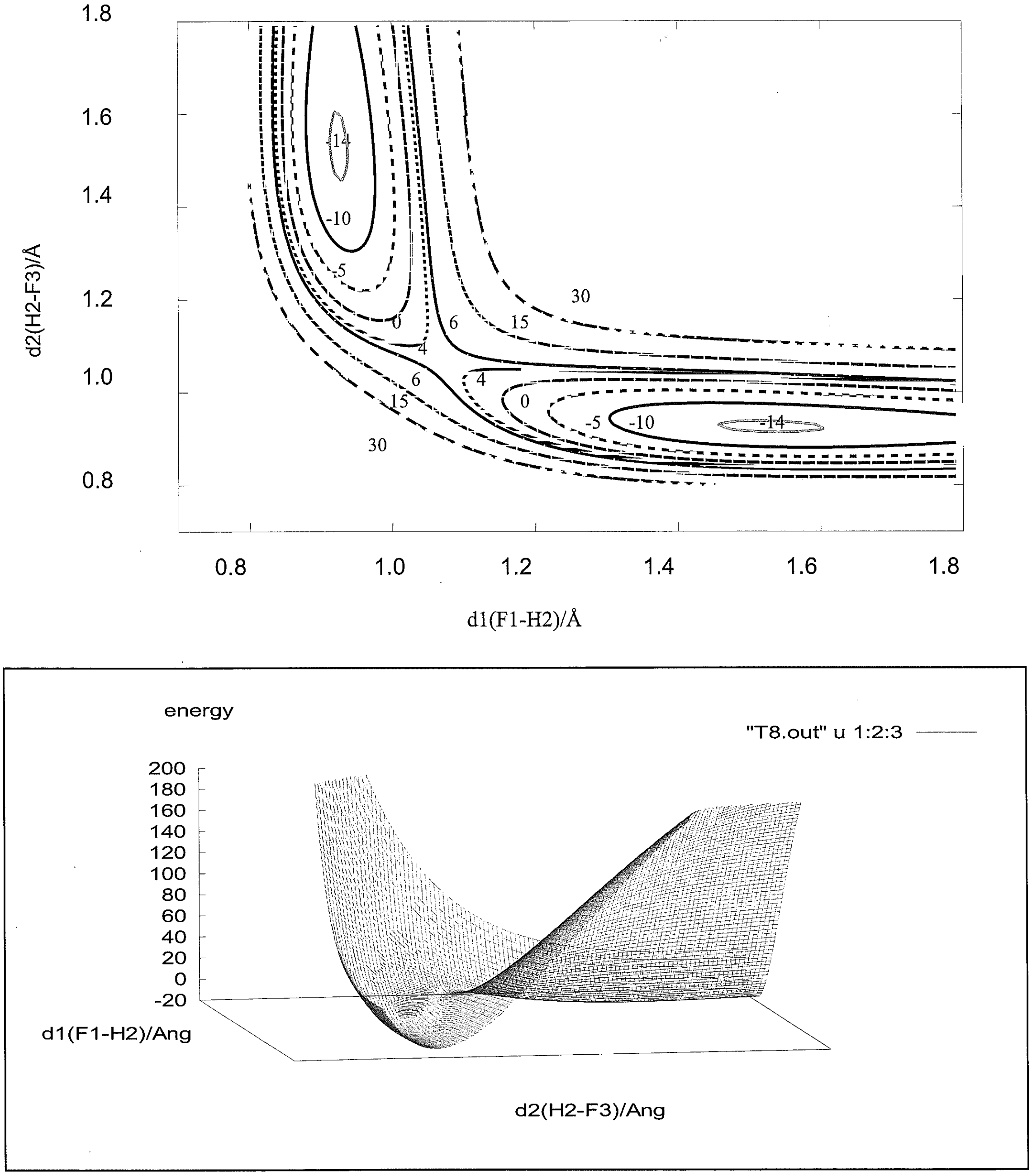

Figure 1. A 2D and 3D view of potential energy surface. The contour levels are expressed in kcal/mol.

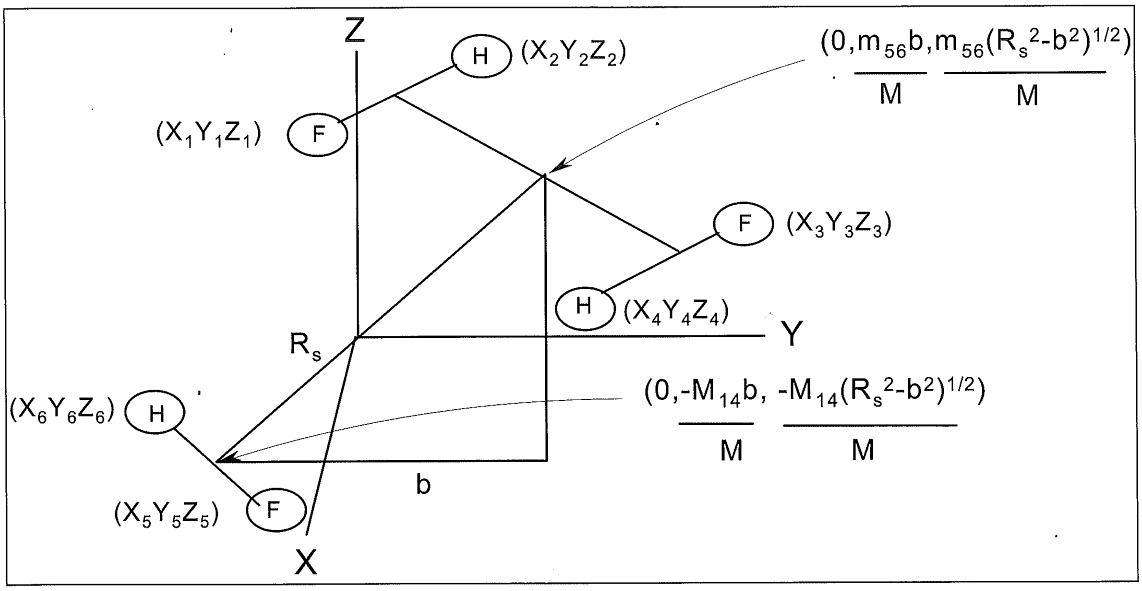

Figure 2. Coordinates of the three HF molecules in the space fixed frame XYZ. R_s is the distance between the CM of $(HF)_2$ and CM of the other HF molecule.
$M_{14} = m_1+m_2+m_3+m_4$, $m_{56}=m_5+m_6$, $M = M_{14} + m_{56}$

Reaction Cross Section

The impact parameter within each stratum is chosen by using stratified sampling. The total cross-section is calculated by summing up the partial cross-sections [23]. The total cross-section is

$$S_r = \sum_b S_r(b) \tag{4}$$

$$S_r(b) = \pi P_r(b)(b_{i+1}^2 - b_i^2) \tag{5}$$

where $P_r(b) = N_r(b)/N_T$ is the reaction probability, N_T = total number of trajectories, $N_r(b)$ = number of reactive trajectories at the specified range of impact parameter, b. The opacity function gives the reaction probability of reaction on collision at a specified impact parameter.

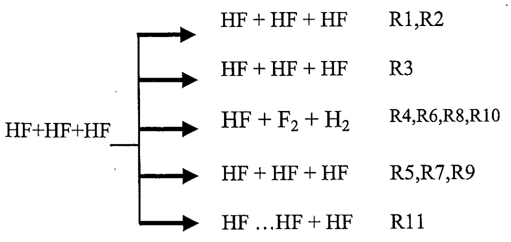

Figure 3. The five different reactions for HF+HF+HF

RESULTS AND DISCUSSION

The QCT calculations on the interaction among the three HF molecules were done using an extension of a software package developed previously [1, 2]. In the present study we have computed over 100,000 trajectories at various vibrational and translational energies. Stratified sampling technique has been used to select the impact parameters randomly at intervals of 0.5 Å and about 1000 trajectories were run at each strata. The energy conservation was in the range 0.000005 to 0.00005 kcal/mol.

A summary of the number of trajectories run for different initial conditions for all reactive channels is given in Table 4. Even with translational energy, E_t of 20 kcal/mol (greater than energy barrier, E_b of 5.5 kcal/mol), there are no 6C reactions taking place at v = 0. Significant number of 6C reactions can be seen happening when the vibrational level is increased to v = 2 although E_t is only 5 kcal/mol. The vibrational energy of each HF molecule at v = 2 is about 28 kcal. The vibrational excitation of all three HF molecules has enhanced the reactivity of the 6C process although E_t is only 5 kcal/mol. For a given vibrational level, increasing the translational energy decreases the monomer exchange reactions (R11). The higher E_t leads to more dissociation of the dimers as well as 4C (or assisted 6C reactions).

Reaction cross sections for the different vibrational and translational energies are given in Table 5. The reaction cross section gives a measure of the interaction between the molecules. A large value indicates a higher frequency of collision hence more likely that a reaction would occur. These results show that the vibrational excitation of the three reactant HF molecules is more efficient in promoting reactivity compared to translational energy.

Figure 6 shows the opacity functions for 6C process at different translational energies, E_t of 5,10 and 15 kcal/mol and vibrational level, v = 2. For v = 2 level, 6C process happens within an impact parameter of up to 3 Å with a high reactivity of around 1 Å for v = 2 level.

A closer look at the detailed trajectories (Figure 6) shows the interesting features of the reaction dynamics. In Figure 6a we have shown the internuclear distances as a function of time for genuine 6C process leading to hydrogen bond exchange between the three HF molecules with initial vibrational states (2,2,2) at E_t=10 kcal/mol. As the reaction proceeds, the distances between the three HF molecules, (12), (34) and (56) increases and the HF internuclear distances of (23), (45) and (16) decreases until they reach the closest distance of approach, which roughly corresponds to the 6C transition state. After crossing the transition state, the internuclear distances of (23), (45) and (16) begin to oscillate around an average distance indicating new bond (molecule) formation.

The behaviour of a typical trajectory for reaction R7 is shown in Figure 6b. In this case the molecules come close to each other at about 10500 timesteps, after which (34) and (56) bonds are broken and new bonds leading to the formation of (36) and (45). Collisions resulting in bond exchange reaction are mainly due to interaction between the incoming molecule (56) and one of the HF molecules (34) or (12) in the dimer. In order for such reactive collisions to take place one of the molecules in the dimer, either (12) or (34) will act as an anchor setting the stage for the incoming molecule (56) to approach and attack the other molecule of the dimer. The anchor will assist in the collision but does not take part in bond formation or bond breaking process. We consider such reaction as assisted 6C reaction although only four atoms are involved in the exchange process.

There are two possibilities of monomer exchange reaction depending on which monomer (12) or (34) is involved in the process. Figure 6c shows the formation of a new dimer (34) (56) when the incoming HF monomer (56) is exchanged with (12). When the collision between the dimer and the monomer results in dissociation of the dimer, three HF molecules are produced (Figure 6d).

In the nonreactive trajectory, the incoming HF molecule (56) bounces off after approaching the HF dimer resulting in no exchange of atoms or dissociation of the dimer. The internuclear distances of (45) and (36) are quite large at the beginning of the interaction, become shorter and later increase again after reaching the closest approach.

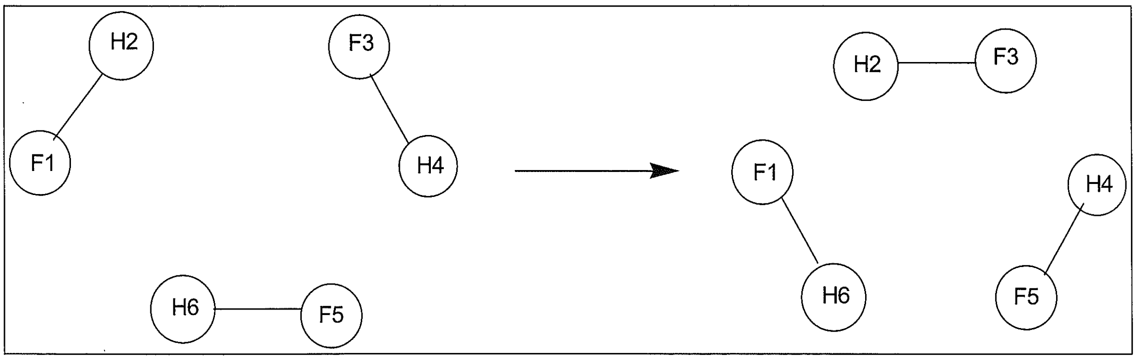

Figure 4. A six-centered (6C) reaction. The numbers used for the reactant molecules are as shown on the left of this figure.

Table 3. Product channels for $H_aF_a + H_bF_b + H_cF_c$ reaction

PROCESS	REACTION	COMBINATION OF ATOMS
Non-reactive	R1	(12)…. (34) (56) H_aF_a …H_bF_b H_cF_c
Dissociation of the HF dimer	R2	(12) (34) (56) H_aF_a H_bF_b H_cF_c
6C reaction forming three HF molecules with H-bond exchange	R3	(23) (45) (16) (25) (14) (36) H_aF_b H_bF_c H_cF_a H_aF_c H_bF_a H_cF_b
6C reaction forming HF, H_2 and F_2	R4	(23) (15) (46) (24) (35) (16) H_aF_b F_aF_c H_bH_c H_aH_b F_bF_c H_cF_a (24) (36) (15) (13) (25) (46) H_aH_b H_cF_b F_aF_c F_aF_b H_aF_c H_bH_c (13) (26) (45) (14) (26) (35) F_aF_b H_aH_c H_bF_c H_bF_a H_aH_c F_bF_c
(56) acts as an energizing partner	R5	(56) (14) (23) H_cF_c H_bF_a H_aF_b
	R6	(56) (13) (24) H_cF_c F_aF_b H_aH_b
(12) acts as an energizing partner	R7	(12) (36) (45) H_aF_a H_cF_b H_bF_c
	R8	(12) (35) (46) H_aF_a F_bF_c H_bH_c
(34) acts as an energizing partner	R9	(34) (16) (25) H_bF_b H_cF_a H_aF_c
	R10	(34) (26) (15) H_bF_b H_aH_c F_aF_c
Monomer exchange reaction leading to the formation of a new dimmer	R11	(12)…. (56) (34) (34)….(56) (12) H_aF_a … H_cF_c H_bF_b H_bF_c …H_cF_c H_aF_a

Table 4. The number trajectories leading to various product channels under different vibrational and translational energies.

VIBRATIONAL LEVEL	ET (KCAL/MOL)	NUMBER OF TRAJECTORIES LEADING TO							
		R1	R2	R3	R5	R7	R9	R11	Tot
0,0,0	5	7172	2534	0	0	0	0	2294	12000
0,0,0	10	7193	3605	0	0	0	0	1202	12000
0,0,0	20	2573	3757	0	0	1	1	668	7000
1,1,1	5	7678	3073	0	0	3	4	2242	13000
1,1,1	10	6956	3771	2	2	10	5	1253	11999
1,1,1	20	3394	3888	1	3	22	25	667	8000
2,2,2	5	7202	4594	27	59	45	46	2024	13997
2,2,2	10	8167	4486	12	28	65	48	1194	14000
2,2,2	20	5948	4163	8	11	110	99	660	10999

Table 5. Reaction cross sections (Å^2) for reactive trajectories R3, R5, R7 and R9

	R3	**R5**	**R7**	**R9**
E5v0	0	0	0	0
E5v1	0	0	0.02	0.02
E5v2	0.12	0.55	0.18	0.23
E10v0	0	0	0	0
E10v1	0.008	0.0016	0.04	0.03
E10v2	0.03	0.32	0.27	0.19
E20v0	0	0	0.001	0.002
E20v1	0.004	0.009	0.07	0.10
E20v2	0.03	0.08	0.35	0.34

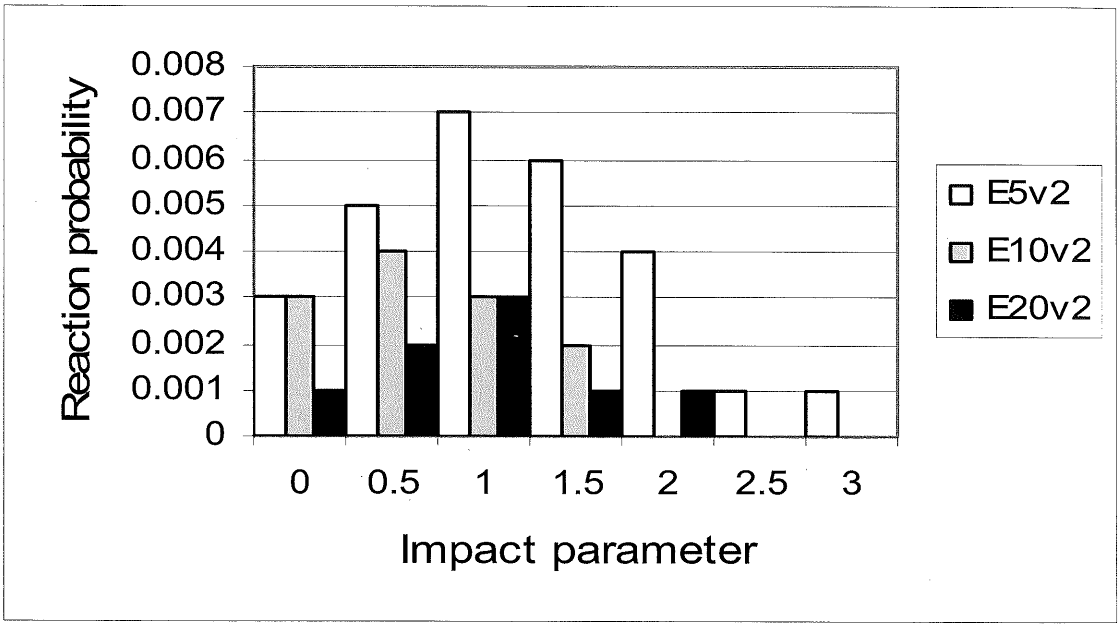

Figure 5. Opacity function (variation of reaction probability with impact parameter) for v = 2 level

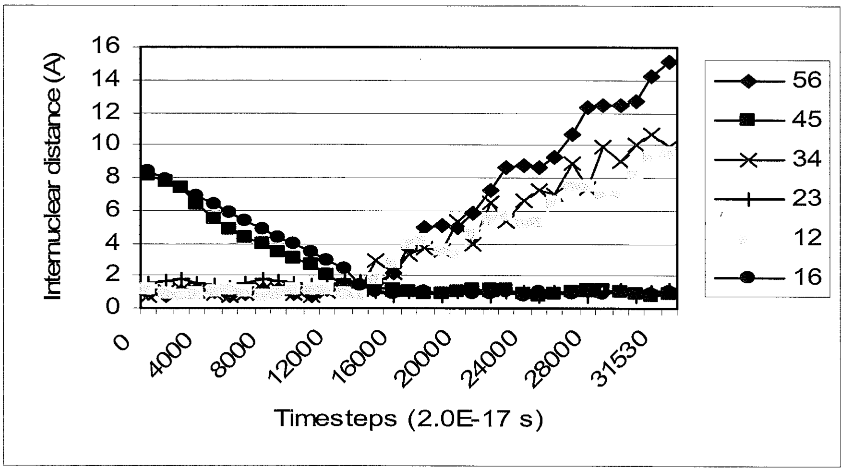

Figure 6a. Typical trajectories for a genuine 6C reaction

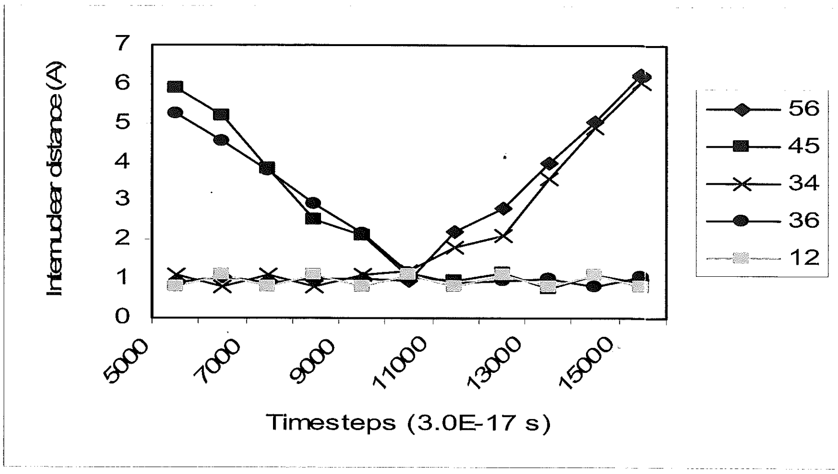

Figure 6b. Typical trajectories for an assisted 6C reaction

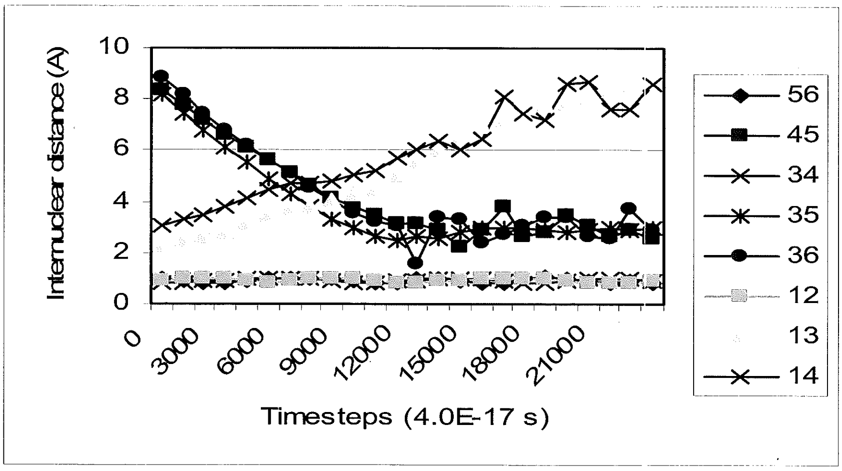

Figure 6c. Typical trajectories for a monomer exchange reaction

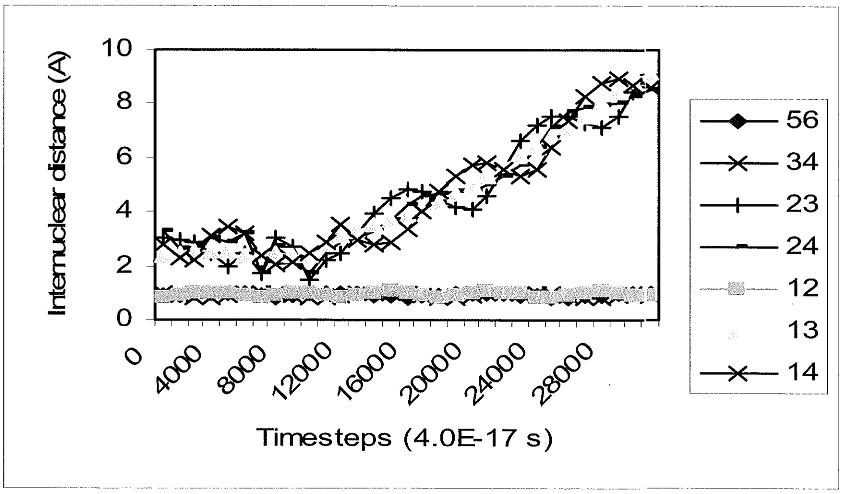

Figure 6d. Typical trajectories for dissociation of dimmer

CONCLUSION

Simulation of a termolecular collision involving three HF molecules has been done on a model PES using the QCT method. Genuine 6C hydrogen exchange reactions do take place but with low probability. Assisted 6C hydrogen exchange reactions also take place with anchoring effect of one of the monomers. Vibrational excitation of the reactant molecules is more efficient than translational energy in promoting reactivity. Further analysis is required to determine product energy distribution, role of reagent rotation and details of the mechanism by which energy transfer process occurs.

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