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Araştırma Makalesi / Research Article

Quantum Dynamic Effects at Insertion Minimum Reaction: H+LiF Reaction

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Abstract
In transition state (TS) region, almost all systems (reactions) have weak van der waals complex structures. When these systems include heavy atom transfer, the forming quantum tunneling effects are suppressed. At TS region these reactions, especially including insertion minimum energy wells, demonstrate to rapidly the formation of product molecules at low temperature region. This study has focused on H+LiF system, one of systems that have this feature. In this system, since unstable H--F--Li complex quasibound states have the barriers in the TS, it is important to investigate and understand to depending on specific quantum states of the initial and the product molecule for this reaction. The results in collision energy range of 0-0.8 eV were obtained and corrected by using Reel Wave Packet (RWP) methods. Integral reaction cross sections as a function of collision energy were calculated via simple J-shifting (SJS) and reaction rate constants were examined in temperature range of 100-1000 ^{0}K.

Keywords: Heavy Atom Transfer, HFLi, Insertion Minimum Reaction, Reaction Dynamics, Transition State.

1. Introduction

The dynamical behaviors of a chemical reaction, in TS region, present much important information about the characteristic of reaction. From experimental point of view, spectroscopic studies are performed in that region where chemical dissociation and combination occur [1]. Particularly, when the reactants interact with each other, that is, the electronic excitation of the system by approaching of atom toward to target molecule causes weak bound system thought to be important spectroscopically. In this case it is important and difficult to get multi-dimensional accurate potential energy surfaces [2]. To this end, chemists have paid attention to the works done for TS region from theoretical point of view. The chemical reactions which have deep wells and heavy atom transfers such as Ca+HF-->CaF+H [3], Mg+HF-->MgF+H [4], Sr+HF-->SrF+H [5], Be+HF-->BeF+H [6], Li+FH-->LiF+H [7] and Ca+HCl-->CaCl+H [8] display long-range interaction model in TS region since the presence of this potential wells which hinder molecular dissociation. In the molecular systems cited above, the heavy F atoms in the ref. 3-7 and Cl atom in the ref. 8 are transferred from reactant molecule to product molecule. Since such reactions have long-range interactions, free radical formations effectively diminish and it is valuable to examine such systems for photoinduced electron transfer reactions because of the spin-orbit coupling on excited systems [9]. However, quantum dynamical calculations performed on such systems need larger grid and propagation time at dynamic calculations since the reactions include heavy atom and the presence of a sudden floppiness on potential energy surfaces. Owing to these factors, it is rather difficult to provide and to fit accurate potential energy surface, as well as to obtain accurate dynamic calculations. Thus, in particular, H+LiF system is theoretically studied more than the above systems since it has a system including less number of electrons [10]. In system including heavy atoms, a great care is necessary to determine some properties of the surface obtained from equilibrium distances, such as the

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deep and the position of energy wells, as well as the altitude and the shape of saddle region consisting on minimum energy path (MEP) [11]. The MEP for this system has been shown detailed in Figure 1.

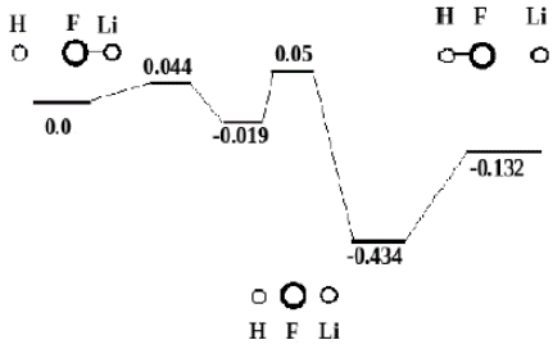

Figure 1. Minimum Energy Path of the System, The energy value of reactants is reference to value of 0 eV. All of energy values have units of eV [12].

Because of the presence of energy barriers on MEP, quantum tunneling effects at low energy region and reaction rate constants at low temperature region are important [13]. In this regard, it was seen that reaction rate constants and reaction cross sections are worth to be examined in this paper. As seen from figure 1, the reaction has two energy wells that are located on both sides of saddle point in TS region. This feature makes this system considerable to research for internal quantum states of molecules formed during the reaction. In such reactions, especially, it is also important to declare the effects both of tunneling on molecular quantum states and of resonances on long-range interactions, respectively.

It would be appropriate to examine chemical reactions that are an entirely quantum mechanical system, with quantum mechanical methods. This work includes RWP method as quantum mechanical method. When molecular structures in reactant channel have large mass, rotational barrier on energy surface becomes small. Thus, the convergence of total cross sections results requires higher J values, and so it has been seen that H+FLi system is more suitable than F+HLi and Li+HF systems to research as theoretical [14]. Since title reaction and its reverse reaction are nearly thermoneutral, it is remarkable to work out this reaction and also has many similarities with Ca+HCl reaction [8]. The paper is organized as follows. The used theories and method are outlined in Sec. II and the results and discussions are interpreted in detail in Sec. III.

2. Material and Method:

The results of time dependent quantum dynamic calculations performed for this reaction are obtained by using RWP method including only real parts of wave packet and analyzed in the asymptotic region of product channel for zero total angular momentum. Since the system includes heavy atom transfer, the calculations contain a large number of grid and CPU time. That is why, coriolis coupling movements that require rather laborious calculations didn't taken into consideration. To get information about distributions of product quantum states, RWP method is used. Further detail information for both methods is found in ref. [15], [21].

The results like cross sections and rate constants can be also obtained with summation of reaction probabilities calculated for needed J values at collision energy range considered.

$$\sigma_{v_0,j_0}(E) = \frac{\pi}{(2j_0+1)k^2_{v_0 j_0}} \sum_{J=0}^{J_{max}} (2J+1)\, P^J_{v_0 j_0}(E) \qquad (1)$$

Instead of solving time dependent Schrödinger Wave equation for all the values of J to obtain scattering probabilities, these reaction probabilities can be calculated by SJS method based on cubic spline approximation, using reaction probabilities for J=0 state and are written as

$$P_{v_0 j_0 K_0}^{JK}(E) = P_{v_0 j_0}^{J=0}(E - E_{shift}^{J}) \tag{2}$$

Here, E_{shift} is the shift in energy for each J calculated and is expressed by

$$E_{shift} = E - BJ(J+1) \tag{3}$$

where, B is rotational constant of reactant molecule in TS region. Reaction rate constants are calculated by taking account to the summation from on all-energy range of cross sections, and so, the dependence of the reaction cross sections on collision energy returns into the change of the reaction rate constant on temperature:

$$k_{v_0 j_0}(T) = \frac{f}{k_B T}\left(\frac{8}{\pi \mu_R k_B T}\right)^{1/2} \int_0^{\infty} \sigma_{v_0 j_0}(E) e^{-E/k_B T} E dE \tag{4}$$

3. Results and Discussions

It is important to determine the contributions of ro-vibrotional distributions of the reactant and the product molecules to reaction probabilities, especially in reactions that have a barrier and insertion minimum energy well in TS region. Title reaction is an important reaction with this feature. Fig. 2 shows the total reaction probabilities calculated by summing over all vibrational and rotational quantum states of product molecule as a functional of collisional energy, and are obtained by changing of specific vibrational (down panel in the figure) and rotational (up panel in the figure) quantum states of reagent molecule. As apparent from figure 1, while some parts of wave packet that are exceeded to the barrier have generated products within a very short time, the others use a large propagation time since presence of insertion minimum in the interaction region, and so, this case have caused the formation of the long lifetimes oscillation structures. Even at the inverse case of this reaction, there are many studies, supporting these results [1, 13, 22]. Once considering studies performed for C+H2 reaction [23, 24] and reactions which have long- lived intermediate cases [25, 26], it should be said that the oscillators decreasing with increasing of collision energy are originated from insertion minimum energy well. Besides, oscillatory structures near threshold region show that this reaction is an indirect and slow reaction, showing the formation of short-lived free radicals in TS region. In such cases, the changes of internal quantum states of reagent molecule have not an important effect on the reactivity and this case has showed the same results as that reported from He+HD reaction studied by Tang and coworkers [27]. Hence, as seen from Fig. 2, the changes of rotational and vibrational quantum states of reagent molecule display similar structures over energy range considered. Furthermore, reaction threshold energy decreases with increasing of the reagent vibrational energy, and reaction exothermic feature has been conserved up to v=3 quantum state since this reaction is nearly thermoneutral. This decreasing has denoted the presence of barrier in the reactant channel and has an important effect on the formation of product molecule in the low energy region. Also a sudden rising in the reaction probabilities decrease with increasing of vibrational energy of reagent and of collision energy.

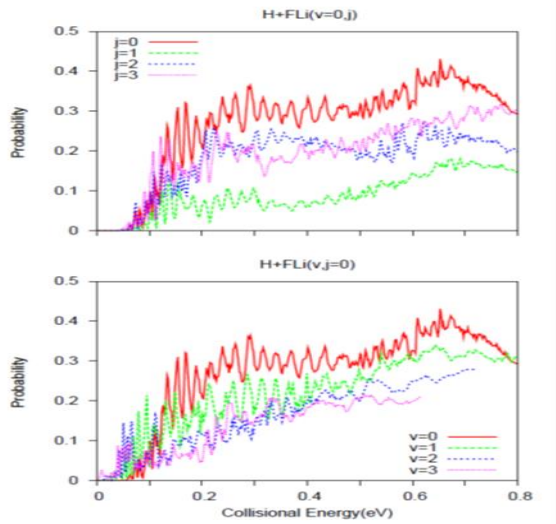

Figure 2. total reaction probabilities for specific rotation (up panel) and vibration (down panel) quantum states of reagent molecule.

While Figure 3 shows the low rotational quantum distributions (up to j'=4) of product HF molecule versus rotational quantum state-selected of reactant LiF molecule, fig. 4 shows the rotational quantum state-specified (up to j'=4) of product molecule against vibrational quantum state-specified of reagent molecule. When compared to fig. 3 with fig. 4, it was seen that the change of rotational quantum state distributions of the product molecule hasn't effectively changed with the increase of rotational quantum states of reagent molecule, but they decrease with increase in the vibrational quantum number of reactant molecule. Also, in fig. 3, odd and even values of rotational quantum states of product molecule separately display similar behaviors to each other. As general, state-to-state behaviors have sharper oscillators than total reaction probabilities (see the figure 2). Once considering all rotational and vibrational states of reactant molecule, reaction probabilities have disappeared about collision energy of 0.4 eV. However, with increasing of rotational quantum number of reactant molecule, this disappearing slightly shifts to higher energy region. Consequently, there is not a clear different among initial quantum states of reagent molecule as expected from insertion minimum reaction.

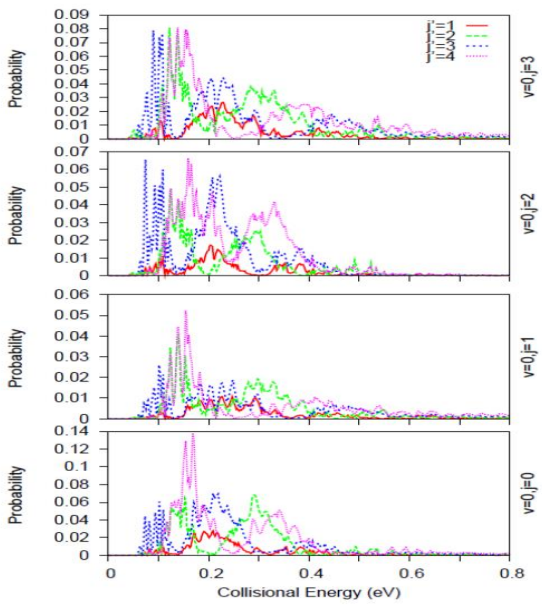

Figure 3. State-to-state reaction probabilities for specific rotation quantum states of reagent molecule.

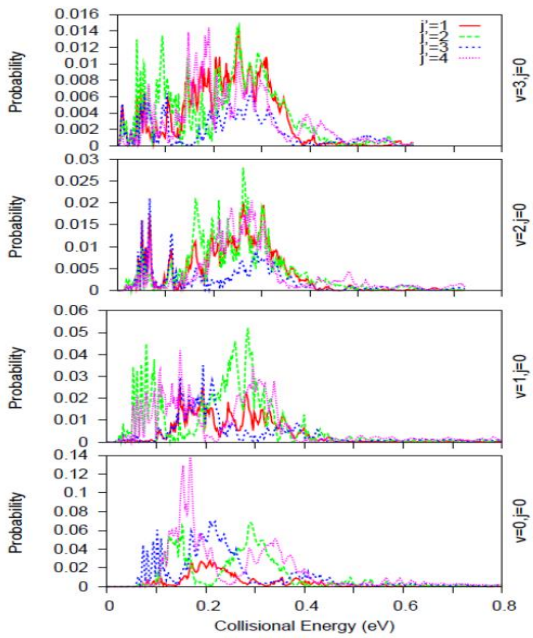

Figure 4. State-to-state reaction probabilities for specific for vibration quantum states of reagent molecule**.**

Resonance structures are proportional to the deep of well in which is located of insertion minimum energy well in the product channel. For this reason, the reaction probabilities in the Ca+HCl reaction performed by Roncero et all [8], having structurally a similar minimum energy path, are sharper than those of this reaction. Fig. 5 displays reaction probabilities for J>0 (only for J=10 and 15 values). In here, the results were obtained with both SJS method performed by using J=0 reaction probabilities results. In such a case, the propagation time required to be fully absorbed of wave packet at end of grid decrease at higher Js. Resonance distributions have spread out to wide energy spacing since this reaction has the long-range interactions and short-lived free radicals in TS region. A similar case was indicated for $H+O_2$ reaction by H. Guo and coworkers [28]. Besides, it was reported by Tang and coworkers [27] who said that centrifugal sudden effect is clearer in high J-values.

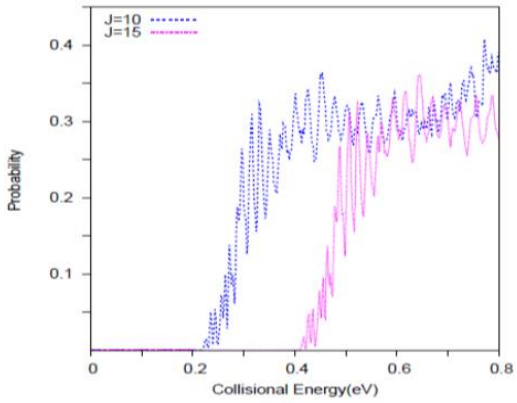

Figure 5. Reaction probabilities for j = 10 and 15 values

It is well known that resonance structures depend on the quasibound van der waals forms in the reactant or the product channel. Such bounds which reduce the effect of centrifugal barrier provide an important contribution to low energy region. As shown in figure6, the resonances structures have increased with further collision energy. The number of J used for the convergence of integral cross

sections results is 19 in collision energy range considered. This case makes this study much simpler to obtain exact quantum dynamic calculations. It should be also noted that quantum tunneling effects in such reactions are suppressed as taking into consideration the last barrier in the figure 1 as cited in the abstract and the introduction of this text.

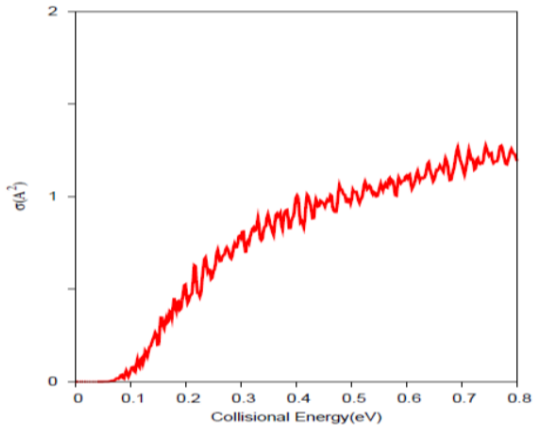

Figure 6. Integral cross sections

Fig. 7 shows reaction rate constants obtained by using results cross sections in temperature range of 100-1000 K. Here it has been clearly seen to what extent reaction rate constants are affected by unstable structures in TS region. Reaction rate constants have been seen very low in the temperature range considered (these constants for fast reaction are in range of 10-9-10-10). At even very high temperature, these values cannot be accessed because of long-lived structures in TS region. In the work performed by Weck and Balakrihnan [7] for this reaction were examined cross sections in the translational energy range of 10-7-10-1 and reaction rate constants in the temperature range of 10-3-103 K. They showed that this reaction display a slow reaction model at temperature range considered due to the relatively heavy fluorine atom transfer. This model is also supported by both barriers in TS region and oscillatory structures in the integral cross sections.

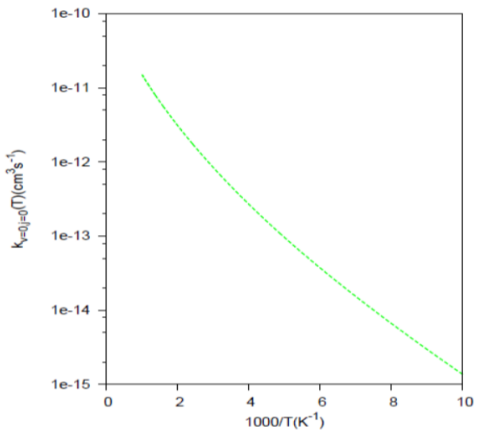

Figure 7. Reaction rate constants

4. Conclusions

In chemical reactions, the basis of dynamics calculations stands on interactions of atoms with each other and moving of atoms on interaction surface. The shortest path passed from a barrier or saddle point on the surface from reactants (product) or products (reactants) is minimum energy path. Barrier and potential wells occurs a basis for quantum mechanical effects. In this work, we observed how the

presence of potential energy wells depends on total angular momentum and internal quantum states of reactant and product molecules. Moreover, in particular, it is also seen that potential wells display important effects for reaction rate constants at low temperatures. Actually, when compared with first barrier one to the second, being on reaction path, both is nearly the same height. In such a case, since reaction has quite weak bounds in that region, it is difficult to determine the effect of the first barrier. But, it may not probably have a strong effect due to heavy atom transfer. For this reaction, also, it would be notable to see how the dissociation or formation of quasibound states affects resonance structures for various isotropic states. Besides, it would be good to compare coriolis coupling and centrifugal sudden results to be calculated for the next paper.

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