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The effect of rotation energies of H_2^+ molecule on the Ne + H_2^+ → NeH^+ + H reaction

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ABSTRACT

The noble gas atoms such as He, Ne and Ar have significantly electronic ionization values around liquid nitrogen temperature (at low temperature values). Because of this feature, the noble gases which are used for some gas detectors, and which is related certain chemical process occurring in the low temperature regions of atmosphere are encouraged to be researched. The chemical reactions subjected to these noble gas atoms have been believed to exhibit important behaviors at the same temperature values. The investigation of their quantum effects in particular energy range and the dependence on temperature of chemical reactions consisting of atom-diatom molecular systems include the subject of reaction dynamics. The title reaction has showed stable structure feature in the interaction region which is the nearest inter-atomic distance. For this reason, it causes to be examined of dynamic effects by depending on quantum states of initial hydrogen ion. The contributions of angular behaviors of hydrogen ion related to total angular momentum and the effects of these behaviors to reaction formations are examined via three dimensional quantum mechanical methods.

Key Words: Noble gas, Zero-point energy, Reaction probabilities, Angular momentum.

1. INTRODUCTION

In order to theoretically verify the scattering calculations in atom-two atom collisions, a realistic potential energy surface of the relevant system must be obtained. The presence of a deep potential well in the transition zone of the colinear collision state of the subject reaction makes it difficult to theoretically examine this reaction [1]. But, because of this transition feature of the reaction, the change in the internal energy of the hydrogen ion molecule in the reaction was explained to be more effective than the transition energy [2]. For Ar and Kr, which are the other noble gas atoms, it is very difficult to do dynamic studies on them since they have non-adiabatic energy surfaces [3]. Coriolis Coupling (CC) and Centrifigual Sudden (CS) calculations were performed in the first dynamic study on the most realistic potential of Ne + H_2^+ reaction. This study was carried out for certain initial vibrational quantum states at the energy range of 0.5-1.5 eV. CC and CS results gave very different results for high total angular momentum values. It was also emphasized that the vibrational quantum state of the hydrogen ion molecule exhibits exothermic character of the reaction at vibrational states that are higher than v = 1[4]. Then the analytical potential energy surface for the same reaction was

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established and the vibrational states of the initial hydrogen ion in certain energies were discussed. However, since this potential energy surface is very similar to the previous energy surface, no dynamic calculations have been made on this potential [5]. By similar to previous work, CC calculations have been made in the range of 0-2.0 eV collision energy over certain vibrational states of hydrogen molecule ion and the resonance states in the obtained cross-sections were discussed. It was also compared with experimental and theoretical results in the literature. A real calculation was made for certain total angular momentum values and then the intermediate values were calculated by the appropriate interpolation method [6]. At the subsequent study, the differential cross sections were also examined again in certain collision energies, which were dependent on the initial vibrational states. It was also discussed the dependence of resonance structures on vibrational states [7]. Another study on the initial vibrational states has also made comparisons over the relevant cross sections of the previous potential energy surface in certain energies. In addition, the internal energy distributions of the product molecule were also evaluated using these energy and potentials, and both potentials exhibited similar behaviors at both high and low energies [8]. The final work on this reaction was the use of deuterium, the isotope of the hydrogen atom, to investigate isotope effects. This work CC and CS calculations were, total cross sections of Ne + H_2^+ and Ne + D_2^+ reactions were investigated by depending on initial vibrational states [9].

In the light of these works done, due to the transitional nature of the potential energy surface, it is emphasized that the initial molecular vibrational and rotational energy states significantly affect the result of the reaction. But, it was not calculated since the rotation energy distributions involve certain computational difficulties. The relevant reaction will be considered in the appropriate vibrational and energy range, and detailed investigations of the effects of different initial rotational energy states on reaction formation will clarify the uncertainties in the literature. At the same time, the effects that occur on the product conditions will be emphasized.

The remainder of work contains the theoretical information needed for the relevant calculations. Finally, the results obtained are interpreted.

2. THEORY

As the formation of free radicals occurs in a very short period of time, usually during femto-second (10^{-15} s), it is very difficult to experimentally measure the information required for the reaction. For this reason, it is very important that the theoretical studies in which solutions containing time in reaction dynamics are obtained. The time dependent Schrödinger equation is used to understand such movements.

$$i\hbar\frac{\partial}{\partial t}\psi(R,r,\theta,t) = \hat{H}\psi(R,r,\theta,t) \qquad (1)$$

If the Hamiltonian operator is time independent, the solution of this equation is written as

$$\psi(R,r,\theta,t+\tau) = e^{-i\hat{H}\tau/\hbar}\psi(R,r,\theta,t) \qquad (2)$$

This equation gives the relation between the function at time t and the function at time t + τ [10]

$$e^{-iH\tau/\hbar}\psi = \{1-(i\hat{H}\,\tau/\hbar)-\frac{1}{2!}(i\hat{H}\,\tau/\hbar)^2 - \frac{i}{3!}(i\hat{H}\,\tau/\hbar)^3+\frac{1}{4!}(i\hat{H}\,\tau/\hbar)^4 ...\}\psi \qquad (3)$$

In the quantum mechanical study of reaction dynamics, the time dependent Schrödinger equation has to be solved for very large propagation times using very small time steps. The excess of the spread term required for convergence of this series leads to an increase in the processor time required at each time step. If the high-order terms in the expansion are neglected, this creates the error at each time step and increases the error amount by increasing the propagation time. Many methods have been developed to solve the time dependent Schrödinger equation until now [11-13]. By means of these developed techniques, many important problems of quantum mechanics such as inelastic scattering, reactive scattering and photo-dissociation can be investigated depending on the time [14]. The Reel-Wave Packet method, developed by Gray and Balint-Kurti, which has been widely used in recent years in solving the time dependent Schrödinger wave equation, allows only the use of the real part of the wave function [15]. The use of only the real part of the wave function reduces the size of the matrices encountered in numeric applications, besides it also severely reduces the propagation time. The above-mentioned equation 2 can be written in trigonometric form as

$$\psi(R,r,t+\tau) = \{cos[\frac{\hat{H}t}{\hbar}] - isin[\frac{\hat{H}t}{\hbar}]\}\psi(R,r,t) \qquad (4)$$

Similarly, the wave function at t is also written in terms of the wave function at t -τ.

$$\psi(R,r,t-\tau) = \{cos[\frac{\hat{H}t}{\hbar}] + isin[\frac{\hat{H}t}{\hbar}]\}\psi(R,r,t) \quad (5)$$

If these two equations are collected to each other, in the form of

$$\psi(R,r,t+\tau) = -\psi(R,r,t-\tau) + 2cos[\frac{\hat{H}\tau}{\hbar}]\psi(R,r,t) \quad (6)$$

is obtained. Since this recurrence relation does not contain a complex expression, the wave function $\psi(R,r,t+\tau)$ is a real function. However, because the equation contains trigonometric expression, it is difficult to use and the Hamiltonian operator to overcome this difficulty is written in form of

$$f(\hat{H}_s) = \frac{-\hbar}{\tau}cos^{-1}(\hat{H}_s) \quad (7)$$

Thus, if the solution function is rearranged,

$$\psi(R,r,t+\tau) = -\psi(R,r,t-\tau) + 2\hat{H}_s\psi(R,r,t) \quad (8)$$

is obtained. In quantum space, the imaginer part of the wave function has no direct effect on the measurable values of the operators corresponding to the dynamic variables. For this reason, the virtual part of the wave function can be subtracted from the above equations. The real and imaginary parts of the wave function, respectively, are

$q = R(\psi)$ and $p = Im(\psi)$ (9)

The spread of wave function in real terms is

$$q(R,r,t+\tau) = -q(R,r,t-\tau) + 2\hat{H}_sq(R,r,t) \quad (10)$$

When considered the destructive potential used to prevent reflection of the wave function from the coordinate interval ends, the spreading scheme is

$$q_{n+1} = \hat{A}(-\hat{A}q_{n-1} + 2\hat{H}_sq_n) \quad (11)$$

Where n=1,2,..,N (iteration step). $\hat{A}$ is the destructive potential. To start the recurrence relation, the first two values must be known and these values are

$q_0 = R[\psi(R,r,t)]$ and

$$q_1 = \hat{A}(\hat{H}_sq_0 - \sqrt{1-\hat{H}_s^2p_0}) \quad (12)$$

Here $\hat{H}_s$ can be scaled in form of $\hat{H}_s = a_s\hat{H} + b_s$. Where $a_s = 2/\Delta E$ and $b_s = -1 - a_sE_{min}$ Looking at Eq. 11, there is only one time effect of the Hamiltonian operator on the wave function. This provides a great advantage in terms of time to reach the desired quantum mechanical quantities [16, 17]. In this method is analyzed the components of the wave function that reach the asymptotic region of the product channel by passing through the strong interaction region of the potential energy surface. These components give information on reactive scattering. Since the wave components pass to the product channel, all scatter information about the product quantum states can be calculated. In this method, an analysis line is selected in the asymptotic region of the product channel and at each time step the wave packet is analyzed on this analysis line and the time dependent coefficients are calculated.

$$C^J_{v_0j_{0,}K_{0,}vjK}(t) = \int q_{vj}(r,\theta)q^J_{v_0j_{0,}K_{0,}vjK}(R = R_\infty,r,\theta,t)drd\theta \quad (13)$$

Fourier transformation of these coefficients gives the energy dependent amplitudes:

$$A^J_{v_0j_{0,}K_{0,}vjK}(E) = \frac{1}{2\pi}\int_0^\infty e^{iEt/\hbar}C^J_{v_0j_{0,}K_{0,}vjK}(t)dt \quad (14)$$

The energy-dependent amplitudes give the elements of the scattering matrix:

$$S^J_{v_0j_0K_0\to vjK}(E) = \frac{-\hbar^2a_s}{(1-E_s^2)^{1/2}}(\frac{k_fk_i}{\mu_{A-BC}\mu_{AB-C}})^{1/2}e^{-ik_fR_\infty}\frac{2A^J_{v_0j_{0,}K_{0,}vjK}(E)}{g(-k_i)} \quad (15)$$

Where k_i and k_f, respectively, are the corresponding wave vector components in the reactant and product channels. μ_{A-BC} and μ_{AB-C} are the reduced masses in reactant and product channels. $a_s$is the energy scaling parameter in Chebychev polynomials. $g(-k_i)$is the components of the initial wave packet with $-k_i\hbar$ momentum. The absolute square of scattering matrix depending on the final and initial quantum states of the reactants and products and the total energy gives the reaction probabilities.

$$P^J_{v_0j_0K_0\to vjK}(E) = \left|S^J_{v_0j_0K_0\to vjK}(E)\right|^2 \quad (16)$$

The sum of the reaction possibilities over all product rotation and vibrational states gives the total reaction probability. Total reaction probability at any energy value [18] is

$$P^{JK}_{v_0j_0K_0}(E) = \sum_v\sum_j P^J_{v_0j_0K_0\to vjK}(\mathrm{E}) \quad (17)$$

3.RESULTS AND DISCUSSION

We obtained the state to state dynamic calculations for the ground state (1^2A’) of the title reaction which was calculated using highly correlated complete active space self-consistent field and multi-reference configuration interaction wave function with a basis set of aug-cc-pV5Z. The subject reaction has a very deep energy floppy in the reaction transition zone and a very high (0.54 *eV*) endothermic energy. Because of these features, very large time spread in the Chebyshev iteration relationship and very high grid steps in the movement of the reacting atoms are needed. Performing real calculations on such reactions is difficult due to both obtaining the relevant potential energy surface and excessive processor effort in the dynamic calculations. For this reason, especially in the high values of j, this difficulty is further increased. In this study, dynamic simulation was performed once the total angular momentum value was zero.

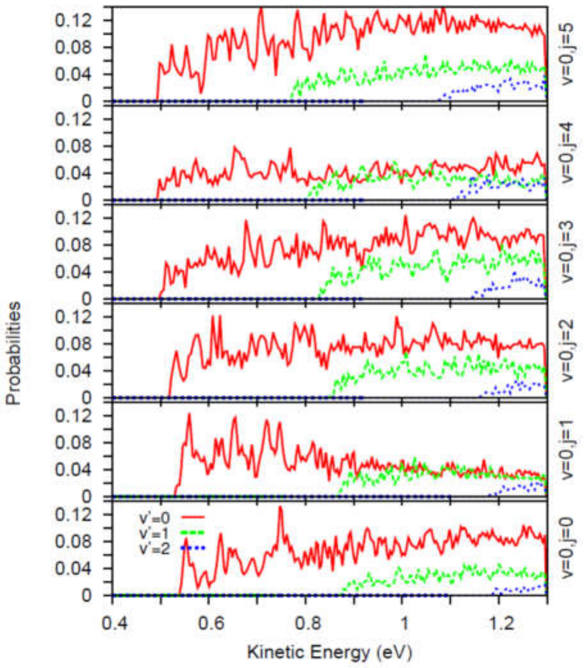

Figure1. The change of the vibrational quantum states of product molecule by depending on the rotational quantum states of the initial molecule.

Figure 1 shows the distributions of vibrational quantum states of the product molecule in certain rotational quantum states (*j=0-5*) of the reactant molecule. Because of the energy floppy at the transition state region in this reaction that occurs in a collinear manner (180^0), reaching grid of wave packets requires a lot of propagation time. Due to these delays, fold reflections occur at the end of the grid and a resonant structure is observed throughout the relevant energy range. In the examined energy range, the product molecule contains only 3 vibrational quantum states. The changes in the vibrations of the product molecule shift to higher energies with increasing quantum numbers of vibrations, as expected. But, the highest contribution of dispersion is seen to be taken from the v '= 0 vibrational quantum state. It is also seen that the reaction occurrences in this quantum state are fast in the threshold region. In this reaction, the changes on the rotation energies of the initial molecule are very prominent at the threshold. These distributions in the graph are the sum of all possible rotational charges of the product molecule.

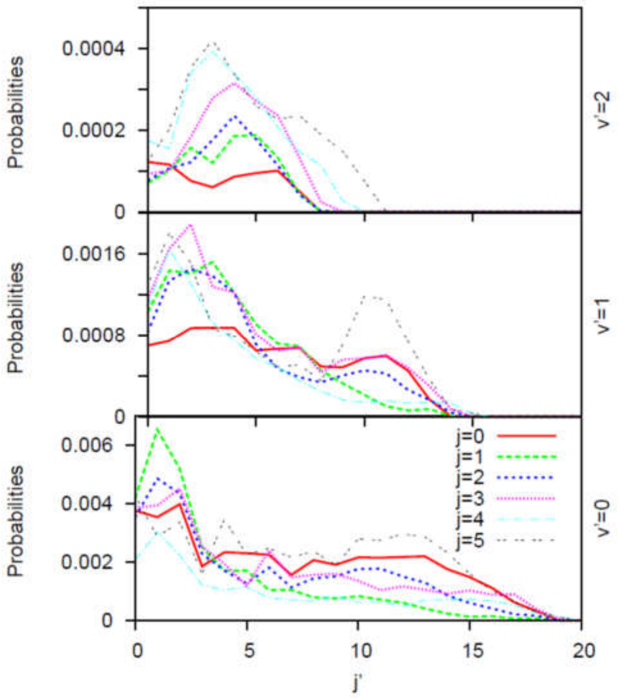

Figure2. The rotation and vibration distributions of product molecule by depending on the rotation quantum states of the initial molecule.

Figure 2 shows the relation of the average of all rotational quantum states of the product molecule to the states of vibration quantum states, in terms of the rotation quantum states of the initial molecule. In the case of v '= 0 vibration quantum, it demonstrates that the contribution of the product rotation quantum state is much. However, a regular distribution of product rotation quantum states was not observed. It is seen that the highest contribution occurs again in the case of v '= 0.

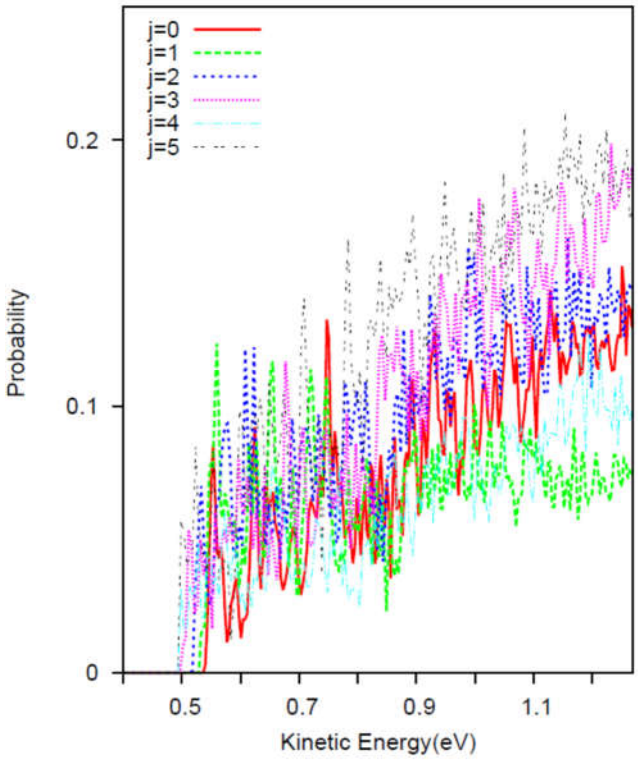

Figure3. The total reaction probabilities depending on the initial rotation quantum states.

Figure 3 shows the kinetic energy dependence of the total reaction probabilities collected over all product vibration and rotational energy quantum states. Because of the minimal energy pathway structure that promotes long distance interactions, vibration and rotation states have a more significant effect on the reaction, rather than the transition energy. Figure 3 showing that the rotational energies are effective and the previous works mentioned in the introduction part showing that the vibrational energies are effective are the best indicators of quantum effects of this reaction. As can be seen in Figure 3, the reaction probabilities depended on the rotation quantum state shows a significant irregularity in the examined energy range. This means that the transition energies are less effective than the rotational energies. The most important criterion for this situation is the barrier on minimum energy path of the system.

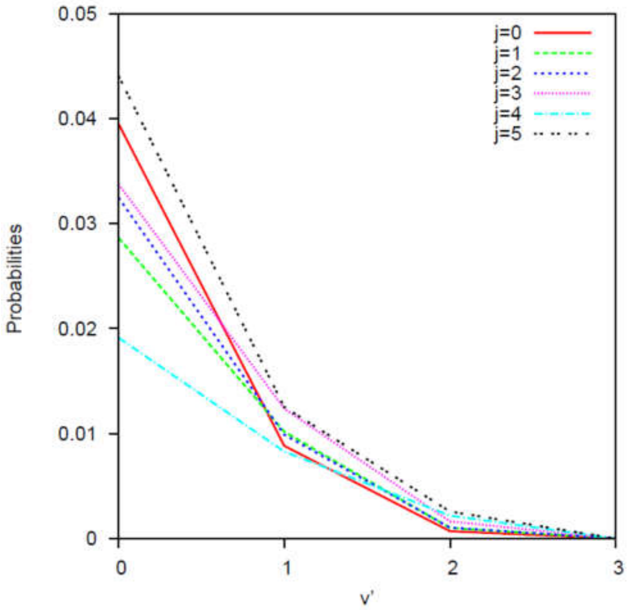

Figure4. The distribution of product vibrational quantum states by depending on the initial rotation quantum states.

Figure 4 shows the total reaction probability summed over all possible quantum states (vibration and rotation) of the product molecule for certain initial rotational energy quantum states. The product vibrational quantum state has a value up to the quantum state v '= 2 in the examined energy range. The increase of the vibrational quantum state of the product molecule has created an undesirable situation to form a new bond in the complex formation (i.e. to form the product molecule). The same case is also valid for the product rotation quantum states in Fig. 2. The increase in rotation and vibration energy of the product molecule supports to increase the related barrier. For this reason, to evaluate higher vibrational and rotational quantum states of the product molecule is possibly by thinking the system at higher transition energy range. Because the threshold energy value that is needed for the corresponding formation shifts towards the higher energy region.

CONCLUTIONS

Due to the endothermic nature of the reaction, the increase in the internal energy of the hydrogen ion shifts the necessary activation energy towards the lower energies, as expected. At the same time, any increase in the internal energy changes of the product molecule shifts the threshold energy generating the title reaction to higher energies. It was observed that the distributions of the vibrational quantum states were very distinct and regular and the rotational energy quantum states were not in a certain regime when they were based on the same transition energy. It has been found that this state does not change depending on the quantum states of the product molecule. In this reaction, it is understood that the initial rotational quantum states do not reflect a distinctive feature in the energy range investigated.

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