Araştırma Makalesi / Research Article

Vibration Dynamics of $H+F_2$ Reactive Scattering

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Abstract
In this paper the vibration distributions of $H+F_2$ reaction on the ground electronic state, which are important for chemical laser, have been examined. The HF molecule formed by this reaction has been examined depending on the initial and final vibration states in particular collision energies. The results have been obtained using time dependent quantum mechanical Real Wave Packet (RWP) method on Potential Energy Surface (PES), which can be given more realistic values in the strong interaction region. The state to state reaction distributions have been calculated to be able to compare with both experimental results at the collision energy of 0.105 *eV* and Quasi-Classical Trajectories (QCT) results depended on LEPS potential at the collision energies of 0.494 *eV* and 0.086 *eV*. Also in this study, the obtained rate constants have been compared by theoretical and experimental values in the literature and are found to be in good agreement with each other.

Keywords: Reaction Dynamics, HF Laser, Reaction Rate Constant, Probability.

$H+F_2$ Reaktif Saçılmanın Titreşim Dinamikleri

Öz
Bu çalışmada kimyasal lazerler için önemli olan, taban elektronik durum üzerinde $H+F_2$ reaksiyonunun titreşim dağılımları incelenmiştir. Reaksiyonla oluşan HF molekülü, belli çarpışma enerjilerinde, başlangıç ve son kuantum durumlarına bağlı olarak incelenmiştir. Sonuçlar, güçlü etkileşme bölgesinde daha gerçekçi değerleri verebilen potansiyel enerji yüzeyi üzerinde zamana bağlı kuantum mekaniksel Reel Dalga Paketi (RWP) kullanılarak elde edildi. Bir durumdan diğerine reaksiyon dağılımları, 0,105 eV luk deneysel sonuçlar ve 0,494 ve 0,086 eV luk Yarı Klasik İz metodu (QCT) sonuçları ile kıyaslayabilmek için hesaplandı. Ayrıca bu çalışmada, elde edilen hız sabitleri literatürde bulunan deneysel ve teorik değerlerle karşılaştırıldı ve birbirleri ile iyi uyumda oldukları belirlendi.

Anahtar kelimeler: Reaksiyon Dinamiği, HF Lazerler, Reaksiyon Hız Sabiti, İhtimaliyet.

1. Introduction

The quantum mechanical methods including to three dimensional the electronic and rovibrotional motions of molecular systems have showed parallel developments together with experimental studies [1]. To get the quantities such as cross sections and rate constants that can be also determined experimentally, it is necessary to detect their electronic energies in all possible configurations of the relevant atoms duration the reaction [2]. But, it is difficult to get exact results for some molecular systems, and it can, thus, cause differences between experimental and theoretical results.

In chemical reactions, especially atom-diatom interactions, the behaviors of unstable structures that occur during the reaction provide important information described by transition state theory. In transition states, the energy transfer through population inversion for specific reactions provides the formation of chemical lasers and natural lasers in the upper atmosphere [3, 4]. For example, on considering HF chemical lasers, the reactions such as $F+H_2 \rightarrow HF+H$, $H+F_2 \rightarrow HF+F$ and $F+HF \rightarrow HF+F$ are most likely atom-diatom reactions in the production of HF molecule [5, 6]. The $H+F_2 \rightarrow HF+F$

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Geliş Tarihi: 16/04/2018 Kabul Tarihi: 29/06/2018

reaction investigated in this study is an important reaction for HF_2 and FHF radical systems which is relevant in development of H_2F_2 lasers. Besides, the reactions involving heavy halogen elements and non-metals like F, Cl and Br which tend to react have been worked as both experimental and theoretical [7,8].

The analysis of experimental results for the nascent molecule has been examined under different energy conditions which are limited at electronically ground state but vibrationally excited state. This process is done by means of the infrared Chemiluminescence emitted from product molecule and declares the ro-vibrational distributions of product molecules, including the subjects of molecular dynamic associated with potential energy surfaces [9]. First experimental study on this reaction has been carried out by Jonathan using Measured Relaxation technique [10]. Later, Polanyi et al. [11] have verified these results using Arrested Relaxation method. Besides, this reaction has also been worked using Chemiluminescence Mapping and Fast Flow techniques [12].

Since title reaction has a rather high exothermic value, it plays an important role on the product quantum states. This study represents to the distributions of the product vibrational quantum state for the specific vibration and collision energies of reagent molecule at total angular momentum J=0 value. The calculations have been done using RWP method and these results have been compared with experimental data obtained by means of Chemiluminescence Mapping and Measured Relaxation techniques that are available in the literature.

The article continues as the follow: In section 2, the relevant theoretical and experimental methods are briefly outlined. In the latter section, the obtained results are compared with previous theoretical and experiment results.

2. Experimental and Theoretical Perspective

IR Chemiluminescence systems measure to the light emitted from the molecular structure formed through a chemical reaction under certain initial conditions. The vibration and rotation motions of the nascent molecular structure are tracked by the detector of laser-induced fluorescence spectroscopy and the reaction rate constants are obtained with discharge-flow and flash photolysis techniques [12, 13].

Theoretically, the information about the distributions of the product quantum state is obtained by the wave functions exceeding to the strong interaction region on the PES. In this case, the wave packet is analyzed by means of the final vibration and rotation quantum states on the analysis line which is an asymptotic distance. So, time dependent coefficients are obtained as

$$C^J_{v_0 j_0 K_0, vjK}(t) = \int \varphi_{vj}(r,\theta)\,\psi^J_{v_0 j_0 K_0, vjK}(R = R_\infty, r, \theta, t)\,dr\,d\theta \tag{1}$$

The time-to-energy Fourier Transform of these coefficients gives to the energy dependent amplitudes, $A^J_{v_0 j_0 K_0, vjK}(E)$. Thus, scattering matrix elements are written in terms of the energy dependent amplitudes

$$S^J_{v_0 j_0 K_0, vjK}(E) = \frac{{}^2 a_s}{\left(1 - E_s^2\right)^{1/2}} \left(\frac{k_f k_i}{\mu_{A-BC}\,\mu_{AB-C}}\right)^{1/2} e^{ik_f R_\infty} \frac{2A^J_{v_0 j_0 K_0, vjK}(E)}{g(-k_i)} \tag{2}$$

Where k_i and k_f , respectively, are the components of the wave vector related with reactant and product channels. μ_{AB-C} and μ_{A-BC} are the reduced masses in the product and reactant channels, respectively. a_s is the energy scale parameter on the Chebyshev polynomials and $g(-k_i)$ is the components of the initial wave packets with $-k_i\hbar$ momentum. Finally, the absolute square of this scattering matrix gives to the reaction probabilities

$$P^J_{v_0 j_0 K_0 \to vjK}(E) = \left| S^J_{v_0 j_0 K_{0\to} \to vjK}(E) \right|^2 \tag{3}$$

The sum of over the all product vibration and rotation states of reaction probabilities creates total reaction probabilities.

$$P^{JK}_{v_0 j_0 K_0}(E) = \sum_{v} \sum_{j} P^{J}_{v_0 j_0 K_0 \to vjK}(E) \tag{4}$$

For any initial quantum state, total reaction cross sections are obtained summing over all possible total angular momentum

$$\sigma_{v_0 j_0 K_0}(E) = \frac{\pi}{(2j_0+1)k^2} \sum_{J} (2J+1) P^{JK}_{v_0 j_0 K_0}(E) \tag{5}$$

So, reaction rate constants are found as

$$k_{v_0 j_0}(T) = \frac{f}{k_B T} \left(\frac{8}{\pi \mu_{Rk_B} T} \right)^{1/2} \int_0^{\infty} \sigma_{v_0 j_0}(E) e^{E/k_B T} E dE \tag{6}$$

Here, k_B is the Boltzmann constant and f is electronic degenerate factor [14].

3. Results and Comments

The title reaction has an exothermic value of -4.43 *eV* and the barrier energy in the reactant channel is 0.135 *eV* with reference to the zero point energy of reactants. Although the PES has a quite high exothermic value, potential energy wells formed by the relevant molecular structures on the reaction path have a shallow surface, which prevents the formation of resonance structures in reaction probabilities. The more information about the PES of title reaction is in detail found in Ref. 22.

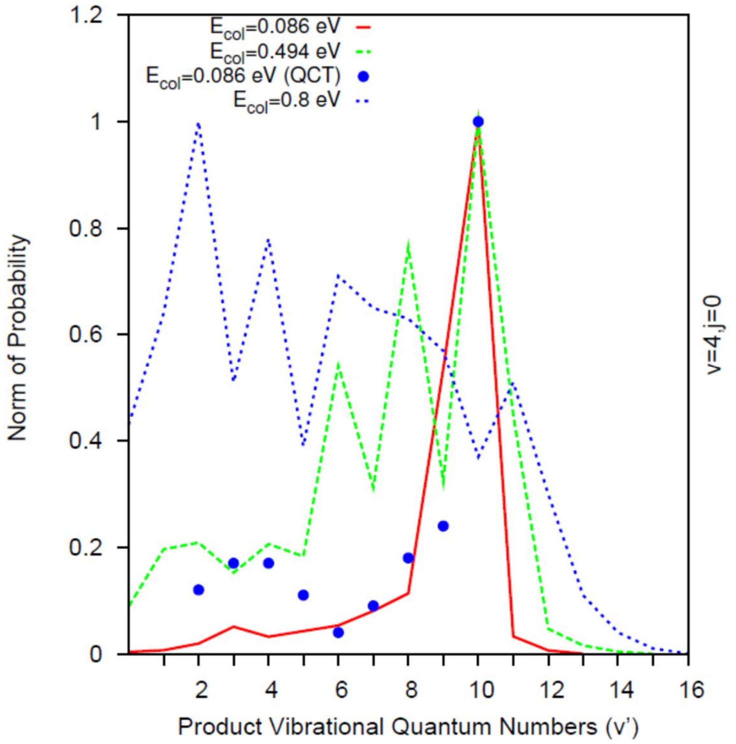

Figure 1. The norm probabilities of H+F_2 (v=4,j=0) → HF +F reaction for specific collision energies

Figure 1 displays the reaction probabilities normalized to the maximum, summed over all rotation quantum states of the nascent HF molecule for v=4 and j=0 quantum states of F_2 molecule. These norms, calculated in the particular energies, have been compared with the normalized probabilities calculated using QCT method on the LEPS potential at collision energy 0.086 *eV* by J. C. Polanyi and coworkers [15]. As shown by Figure 1, v'= 6., 7., 8. and 10. quantum states of the product molecule in the QCT calculations have been seen to be in good agreement with the present results. The similar behaviors have also been exhibited at lower quantum states (v'= 2., 3. and 4.). When the higher energy regions are considered, the resonance structures of probabilities for the relevant product quantum state have been increased in good agreement with collision energy. The maximum population in the collision energies of 0.086 and 0.494 *eV* have been seen at v'=10 quantum state, but the one in the higher energies have been at v'=2 vibration quantum state. Also, the needed product vibrational quantum numbers have increased with increasing energy.

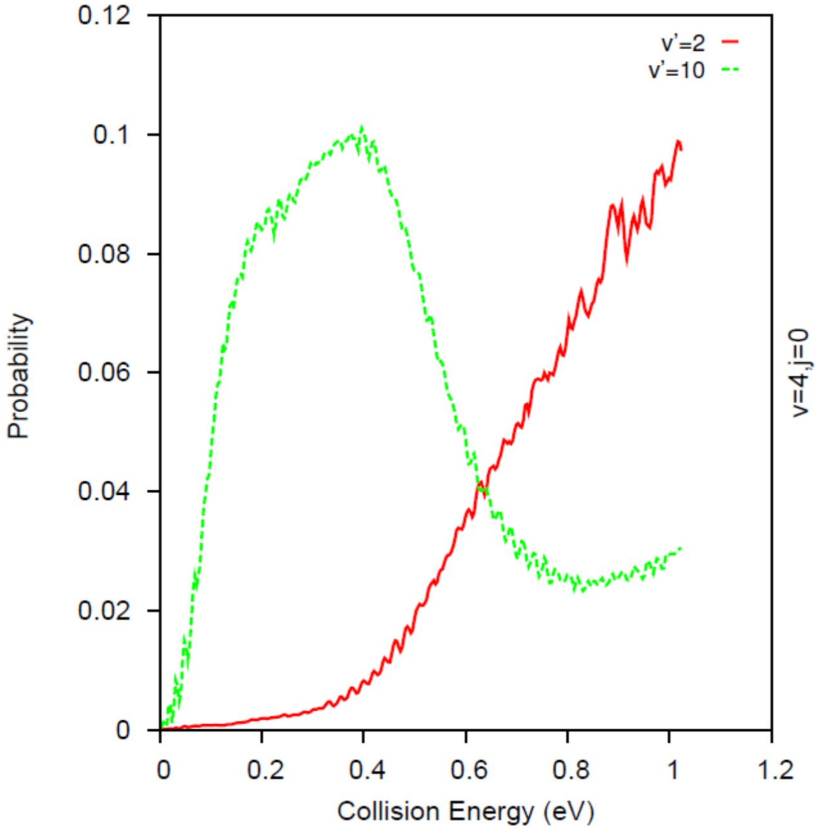

Figure 2. The reaction probabilities for the v'=2 and 10 quantum values of the product molecule

The dependent of product vibrational quantum numbers on collision energy for the same initial quantum states has been seen in Figure 2 in detail. As shown from Figure 2, the distributions of reaction probabilities up to collision energy of about 0.6 e*V* have shown the maximum probability at v'=10 vibration quantum state while the reactivity in the values which are higher than this energy is stronger at v'=2 quantum state (No other quantum states needed to be showed).

Figure 3 shows the same energy situations as in Figure 1 but v=0 and j=0 quantum state of the reagent molecule. The calculations are compared with Polanyi's [15] results obtained via QCT method. These distributions in the different energies have showed the similar behaviors. When compared to Figure 1, the vibration quantum state of the reagent molecule for this reaction plays an effective role on the reactivity. The results of QCT and RWP methods have a good accordance with maximum population (v'=5). But most of the other values have significant deviations. When Figure 3 compared with Figure

1 in the energy range from 0 to 1 *eV,* the maximum distributions for the v=4 state of the reagent molecule are in v’=2 for high energies and v’=10 values for low energies while the maximums for the v=0 quantum state are in v’=5 value for high energies and v’=6 value for low energies. That is, the reactivity with the increase of vibration quantum number of the reagent molecule spread out a broader product quantum range.

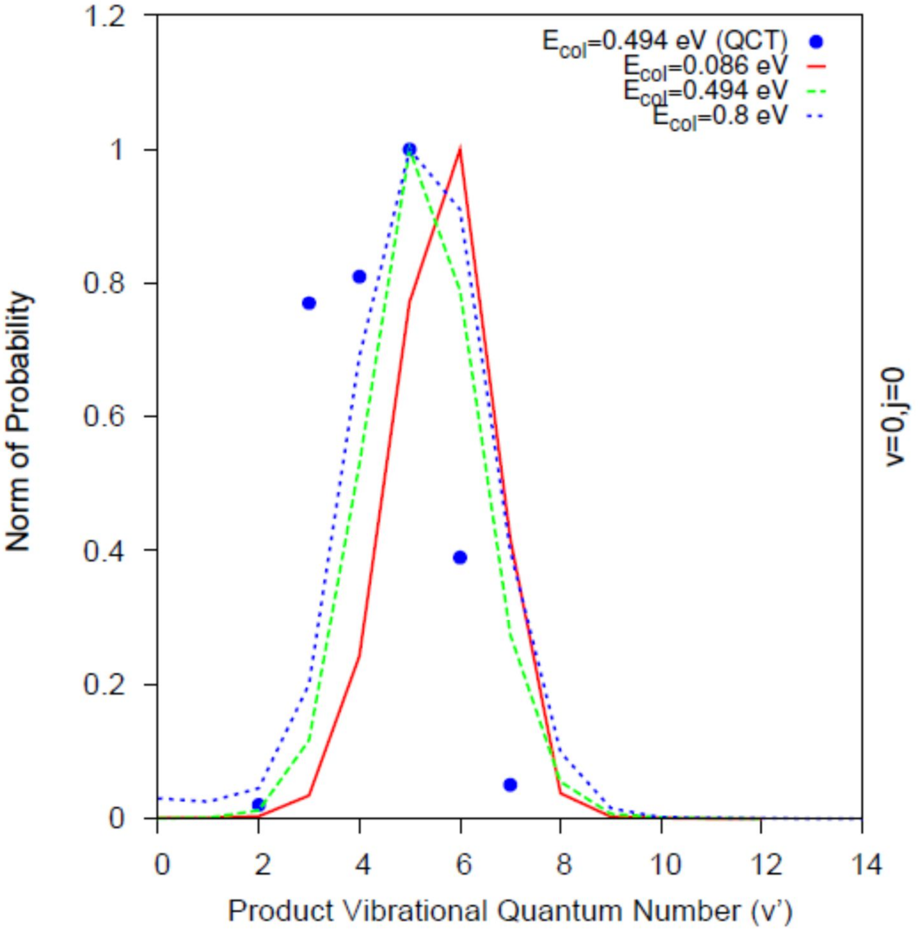

Figure 3. The product vibration quantum distributions of H+F_2 (v=0,j=0)→ HF (v’)+F reaction

Figure 4 shows the norm probabilities of the vibration quantum distributions of the product molecule in the collision energy of 0.105 *eV* for the ground energy state of reagent molecule and compares present results with two experimental results in the literature. The results of Chemiluminescence Mapping Pressured Pulse technique used by D. C. Tardy et al [16] (shown as ‘exp’ in the figure) and of Measured Relaxation method used by N. Jonathan et al [17] (shown as ‘exp-2’ in the figure) have been compared with the present calculations. The present results are found to be in a better fit with that of N. Jonathan, in especially low-amplitude regions of the peak. The experimental results examined in this figure can be only calculated for the results that are greater than v’=1 value. In the RWP method, it gives the result for v’=0 value, but since this value has very small scale it has not seen in the graph. As is also seen in Figure 3, the maximum population in the low energies reveals at v’=6 quantum state. These experimental results occur by transformation of emission intensities to population densities via Einstein coefficients. Thus, the causing of the differences between the experimental results is the efficiency of radiation obtained by these coefficients.

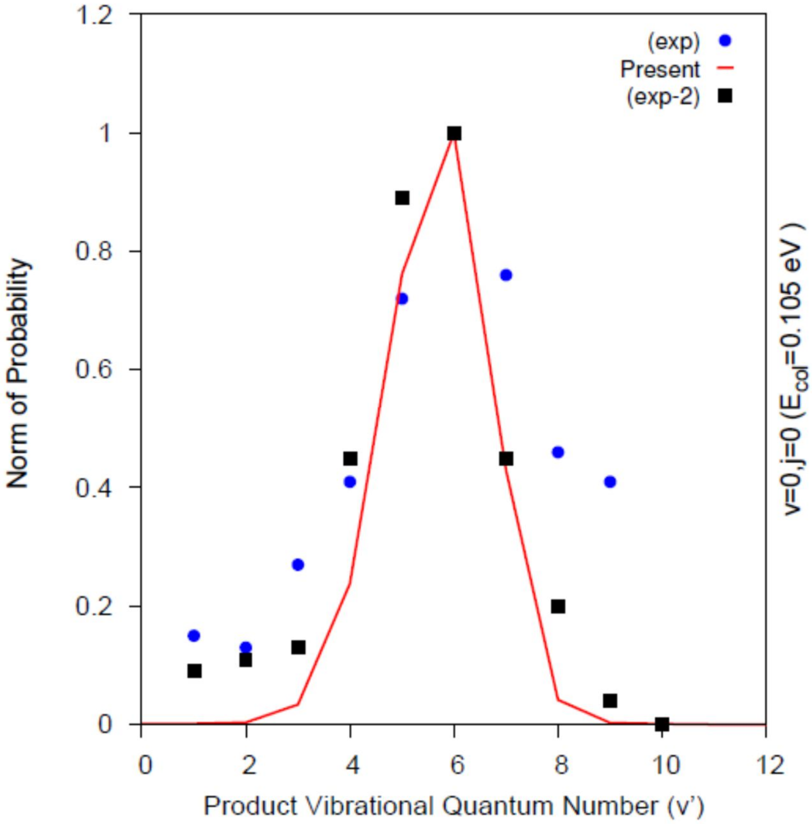

Figure 4. The product vibration quantum state distributions of $H+F_2(v=0,j=0) \rightarrow HF(v')+F$ reaction at collision energy of 0.105 *eV*

Figure 5 gives the reaction rate constants on the temperature, ranging from 1 to 1000 K. On the experimental side, the results of R. G. Albright et al [18] and K. H. Homman et al [19] and the results of Connor et al [20] and Wilkins et al [21] used QCT method on the LEPS potential for theoretical perspective have been used for comparison with the present results including to the all vibration quantum states (from 0 to 10) of the reagent molecule (shown with ”i” subscript) and the all vibration quantum states (from 0 to 19) of the product molecule (shown “f” subscript). For this reaction, the work some of us [22] has published has shown the v=0 quantum state of the reagent molecule to obtain the reaction rate constants. The results including the only v=0 quantum state are averagely 5 times less than that of Homman while the present results are about a quarter of that of Homman. This case has showed that the initial vibration quantum numbers have an important effect on the reactivity. The present results are averagely in good agreement with that of Homman which is more reliable that other results [23] in the considered temperature range, but are in a reasonable value with the results of Albright and the other theoretical at room temperature. Also the contribution of the vibrational quantum states of the product molecule is more efficient than that of the reactant molecule and gives more consistent results with Homman's results.

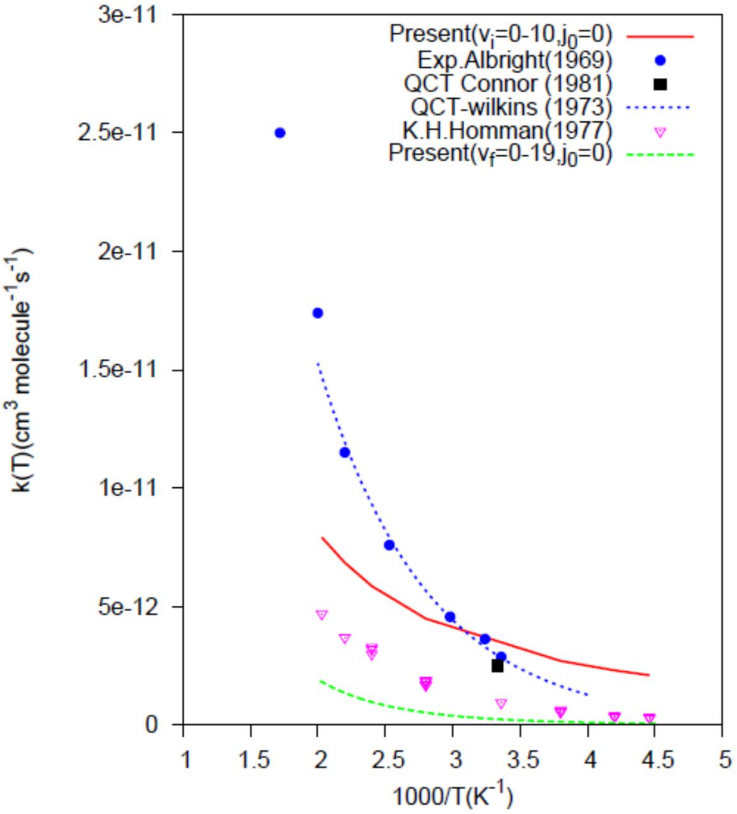

Figure 5. The reaction rate constants versus (1/T)

4. Conclusions

The behaviors of reaction probabilities and resonance structures occurred in state-to-state probabilities of title reaction have effectively depended on the initial vibrational quantum number rather than the collision energy. This dependence has also been understood from the reaction rate constants. When compared the present results with QCT results, they are much closer to experimental values. This case has showed to be more realistic of the PES used in the present work. State-to-state reaction probabilities for title reaction together with the used PES should be re-calculated by using Coriolis Coupling method to see the effect of total angular momentum.

5. Acknowledgements

The authors are grateful to Prof. G. G. Balint- Kurti for his guidance and to the Scientific and Technological Research Council of Turkey for TR-Grid facilities.

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