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REGULAR ARTICLE

Quantum Wave Packet Dynamics of the N(^{2}D) +H_2 Reaction

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Abstract: In this work, the N+H_2 (ν,*j*) reactions have been studied by means of quantum mechanical real wave packet method on an ab initio potential energy surface (PES) newly modified by Yang et al. [J. Phys. Chem. A 2013, 117, 3-8]. First accurate total and state-to-state reaction probabilities at total angular momentum J=0 have been calculated in a broad range of collision energies. Final state resolved reaction probabilities and product ro-vibrational distributions have been calculated at *J*=0. Initial state integral cross sections have been calculated by using Centrifugal Sudden approximation considering every total angular momentum without using any interpolation method. The effects of initial rotational and vibration on the dynamics have been also investigated. The obtained integral cross sections have been compared with the available data in the literature.

AMS subject classifications: 81U10, 81V45

KeyWords: State-to-state reaction probabilities, Centrifugal sudden, integral cross sections

Introduction

From atmospheric perspective, N+H_2 reaction is important to be understood the chemical processing of combustion systems that occurred in solar system, interstellar medium and molecular clouds. Especially, the compounds, involved metastable N(^{2}D) atom in these environments, are quite abundant and lead to various reactive scattering since the excited one

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is to be more reactive than the ground one[1-4]. The title reaction plays a central role in both experimental [5-6] and theoretical atmospheric point of view.

The first theoretical study on potential energy surface (PES) of title reaction was performed by H. Kobayashi and coworkers [7]. In that work, quasiclassical trajectory (QCT) studies were carried out to test of the potential energy surface. Then, Pederson et al. [8] reported the first global potential energy surface of this reaction that has been considered as prototypes of insertion reactions and has a deep potential well in transition state region with a small barrier in the entrance channel, on the contrary to the other insertion reactions[9]. Balucani and coworkers [1] implemented quantum mechanical, statistical and quasiclassical methods on the PES of Pederson [8]. Later on, Ho et al. improved the potential energy surface of Pederson and carried out QCT calculations [10]. There are many theoretical works in the literature on the N+H2 reactive scattering process [11-13].

The PES used in the present work, has been reported by Yang et al. [14] recently. This PES is based on an analytical function that gives more accurate results in the range of small internuclear distances when compared to the other previous surfaces mentioned above [14]. More detailed information for this PES can be found in ref. [14]. Since the NH_2 reaction, especially, has a deep well in the transition state region, NH_2 complex structure involves long-lived intermediate which tends to be an indirect reaction. In such reactions, the distributions of the internal quantum states of product molecule have been worth of being explored.

In this study, total and state-to-state accurate reaction probabilities, specific-initial and -final quantum state distributions of reactant and product are examined by means of a Real Wave Packet Method. This method is briefly outlined in section 2. The obtained results are discussed in part 3 of this text.

Theory

The method employed in this work is based on the use of real wave packet method, as originally introduced by Balint Kurti and Gray [15]. The time-dependent Schrödinger equation in Jacobi coordinates,

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

The Hamiltonian for total angular momentum J=0 is expressed in terms of the Jacobi coordinates as

$$\hat{H} = -\frac{\hbar^2}{2\mu_R}\frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2\mu_r}\frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2}\left(\frac{1}{\mu_R R^2} + \frac{1}{\mu_r r^2}\right)\frac{1}{\sin\gamma}\frac{\partial}{\partial\gamma}\sin\gamma\frac{\partial}{\partial\gamma} + V(R,r,\gamma) \tag{2}$$

Where *R* is the distance between the center of mass of the diatomic subunit (H_2) and the atom (N) and r is the internuclear distance of the diatomic molecule (H_2) in the reactant channel and is the angle between *R* and *r*. In atom-diatom reactive scattering problems the atom and diatom subunit will change from reactants to products and therefore the definition of the Jacobi coordinates will change correspondingly. The atom and diatomic will be H and NH in the case of products. μ_R and μ_r are the reduced mass of the atom-diatomic molecule and diatomic molecule respectively in reactant or product channel.

In this study, equation (1) is solved in Jacobi coordinates for total angular momentum *J*=0 then centrifugal sudden approximation is implemented to calculate reaction probabilities J larger than zero, *J*>0. The grids used for the internal coordinates are listed in **Table 1**, and they have been determined after a careful convergence test of the reaction probabilities at *J*=0.

In the real wave packet approach, the Hamiltonian operator is modified as

$$f(\hat{H}_s) = -\frac{\hbar}{\tau}\cos^{-1}(\hat{H}_s) \tag{3}$$

where $\hat{H}_s = a_s\hat{H} + b_s$ with a_s and b_s chosen to ensure that the minimum and maximum eigenvalues of $\hat{H}_s$ in the interval (-1,1). The scaled Hamiltonian,$\hat{H}_s$ is used by Tal-Ezer and Kosloff in Chebyshev expansion of the propagator [16] where each step requires only a single evaluation of the action of the Hamiltonian on a (real) vector. This approach shares many features with the work of Kouri and co-workers [17, 18] Mandelshtam and Taylor [19, 20] Kroes and Neuhauser [21] and Chen and Guo [22, 23] and Roncero et al. [24]. This scaling is necessary to provide that the mapping in equation (3) is single valued. Thus modified time dependent Schrödinger equation can be given in general form as

$$f(\hat{H})\psi(R,r,\gamma,t) = i\hbar\frac{\partial\psi(R,r,\gamma,t)}{\partial t} \tag{4}$$

The initial wave packet is set up in reactant Jacobi coordinates,$\Psi(R_\alpha, r_\alpha, \gamma_\alpha, t)$, and then is transformed to product Jacobi coordinates, $\Psi(R_\beta, r_\beta, \gamma_\beta, t)$. The initial wave function can be written as

$$\psi(R_\alpha, r_\alpha, \gamma_\alpha, t) = e^{-ik_0(R_\alpha - R_{0,\alpha})}e^{-\beta(R_\alpha - R_{0,\alpha})} \times \frac{\sin[\alpha(R_\alpha - R_{0,\alpha})]}{R_\alpha - R_{0,\alpha}}\varphi_{v,j}(r_\alpha)P_j(\cos\gamma_\alpha) \tag{5}$$

where $\varphi_{v,j}(r_\alpha)$ is the vibrational and $p_j(\cos\gamma_\alpha)$ is the rotational components of the wave function. The $e^{-ik_0(R_\alpha - R_{0,\alpha})}$component gives an initial momentum to the initial wave function.

The wave packet is analyzed at each time step in the asymptotic region of the product channel and state-to-state reaction quantities are obtained as a function of collision energy depending on the S matrix elements [24, 25] as

$$P_{v,j}^J(E_c) = \frac{1}{2\min(J,j)}\sum_k \sum_{v'j'k'} \left|S_{v'j'k',vjk}^J\right|^2 \tag{6}$$

Here the quantum numbers without prime (v', j, k) are associated with the reagent diatomic molecule, while the presence of the prime (v', j', k') is associated with the product fragment of diatomic molecule.

A quite approximate way to calculate reaction probabilities for *J*>0 is to use the centrifugal sudden approximation which significantly reduces the amount of computational effort with respect to the Coriolis coupling calculations. Once the reaction probabilities are calculated for all the total angular momentum larger than zero, total integral cross-sections are calculated by summing partial waves over all J values as

$$\sigma_{v,j}(E_c) = \frac{\pi}{k_{v,j}^2} \frac{1}{2j+1} \sum_{J=0} (2J+1)[2\min(J,j)+1] P_{v,j}^J(E_c) \tag{7}$$

Results and Discussion

The total reaction probabilities at *J*=0 for the initial rotational (ν=0, *j*=0-3) and vibrational (ν=1, 2, *j*=0) states are shown in **Figure 1** as a function of collision energy. As can be seen, in all the cases considered, the reaction probabilities start with a threshold as expected from an exothermic reaction with barrier and then show a sudden increase, reaching an average value of 0.9. The initial rotation and vibration states of reagent have a big effect on the reactivity at least for *J*=0. This effect seems to decrease with increasing collision energy as seen in the top panel of **Figure 1**. In all cases reaction probabilities display broad oscillatory formations in the whole range of collision energy in agreement with one of our previous calculations on the PES of Ho et al. [10].

Figure 2 shows the product rotational state resolved reaction probabilities as a function of collision energy in a range of 0-1.0 eV collision energy for the initial specific quantum states (ν=0, *j*=0-3) of reagent molecule. In general, the *j′* state-resolved reaction probabilities show more resonances than the total one. The low product rotational quantum states of the NH molecule for each initial rotational states of H_2 (*j*=0-3) display similar structures. Reaction probabilities increase with increasing product rotational quantum states as clearly shown in **Figure 2**. The contributions of these products rotational states to the total reaction probabilities are quite insignificant when go to the high product rotational quantum states (not shown here).

Figure 3 shows state-to-state reaction probabilities as a function of collision energy for the initial vibrational states (ν=0 and 1) of the H_2 molecule. Oscillatory behavior persists in all reaction probabilities. The reaction probabilities for ν=1 excited state have a sharper oscillatory in threshold region when compared to the ground state of ν=0. These oscillatory behaviors are supported by deep well in the potential.

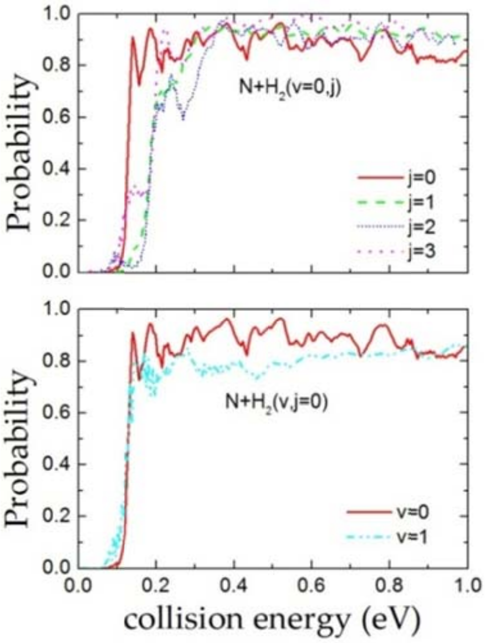

Figure 1: Total reaction probability as a function of collision energy. Top panel: the effect of initial rotation. Bottom panel: the effect of initial vibration.

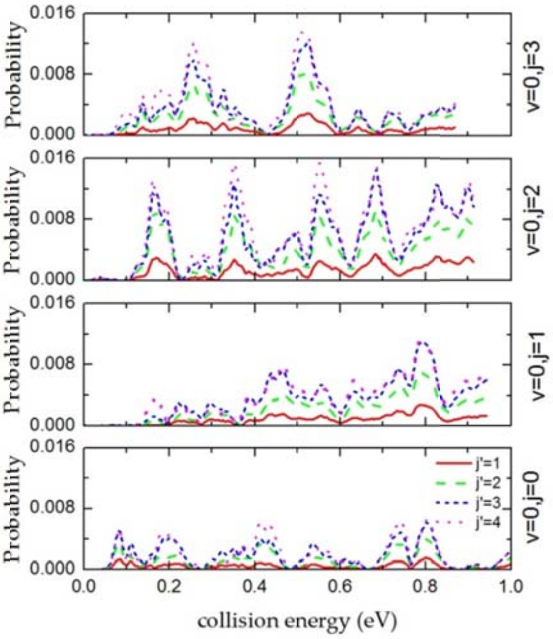

Figure 2: Product rotational reaction probability as a function of collision energy for initial rotational state of H_2 molecule.

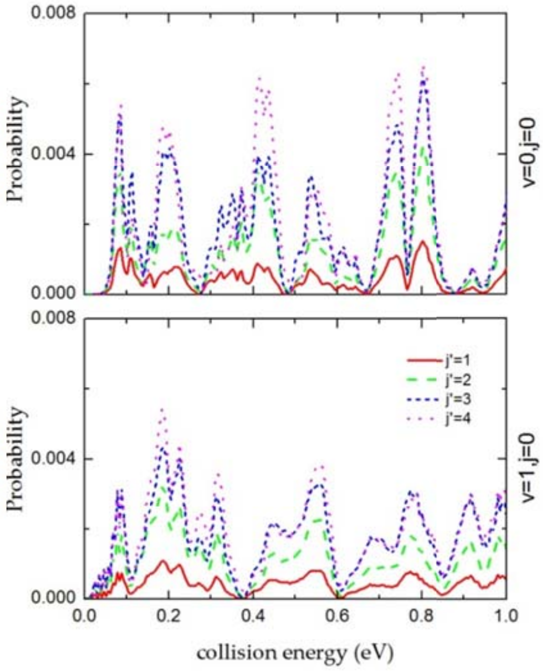

Figure 3: Product rotational reaction probability as a function of collision energy for initial vibrational state of H_2 molecule.

Figure 4 shows the vibrational reaction probability distributions averaged on the studied range of collision energy for some specific initial ro-vibrational state of reagent molecule. These distributions are obtained by summed over all -*j*′ values. With this figure it is important to point out that the calculations for total angular momentum larger than zero to obtain total cross section someone should consider at least ν′=7 product vibrational quantum numbers depending on the initial states. On the other hand, the available vibrational quantum state of product molecule increases with increasing vibrational quantum number of reagent. In all cases, reaction probabilities decrease with increasing product vibrational quantum numbers. One of notable states in this figure is that the transition from the ν=1, *j*=0 state of reactant molecule to the ν'=1 state of product molecule has strongly effected on the formation of reaction when compared to the other states.

Reaction probabilities for *J*>0 have been calculated by using centrifugal sudden approximation and displayed in **Figure 5** at selected total angular momentum, *J*. As can be seen, as *J* increases reaction probabilities shifts towards larger collision energies and oscillation behaviors persist on all the reaction probabilities. To calculate integral cross sections, the contribution of all the partial waves should be considered in the collision energy

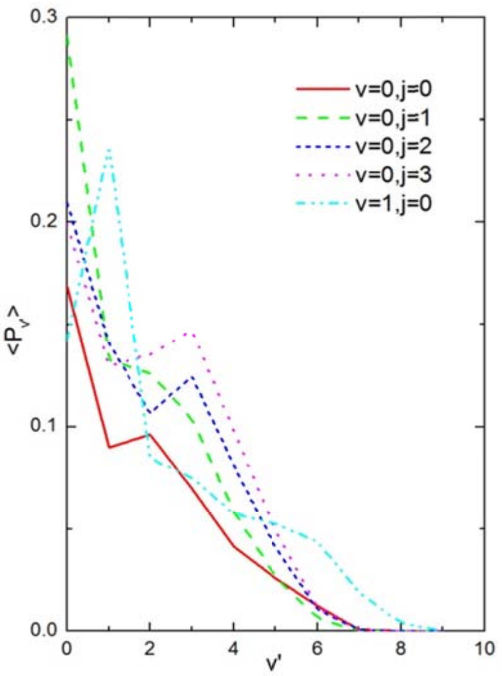

Figure 4: Product vibrational state distribution averaged on collision energy as a function of initial ro-vibrational state of reagent molecule.

range of studied. From threshold to 0.4 eV it was necessary to have 40 partial waves to converge integral cross section. Wave packet calculations have been done for each total angular momentum quantum numbers *J*'s, from *J*=0 to *J*=40 by using Centrifugal Sudden Approximation (CSA) and summed to obtain integral cross section. **Figure 6** depicts the total integral cross section (ICS) as a function of collision energy. ICS increases with increasing collision energy and shows a threshold like an endothermic or a reaction with barrier. The agreement between present ICS and the previous one calculated on the PES of Ho et al [10] using an accurate wave packet method [26] and simple J-shifting approximation [11] are excellent at very low collision energy (from threshold to 0.15 eV) and then start to deviate. Present ICS displays a large oscillation in the range of 0.15-0.25 eV collision energy, but this behavior is not persisting on the previous calculations implemented on the PES of Ho et al. [10]. This is a characteristic behavior of the PES used in this work. More detailed and accurate calculations should be done to find out the difference between the present and the previous dynamics calculations. Our efforts in this side are currently in progress.

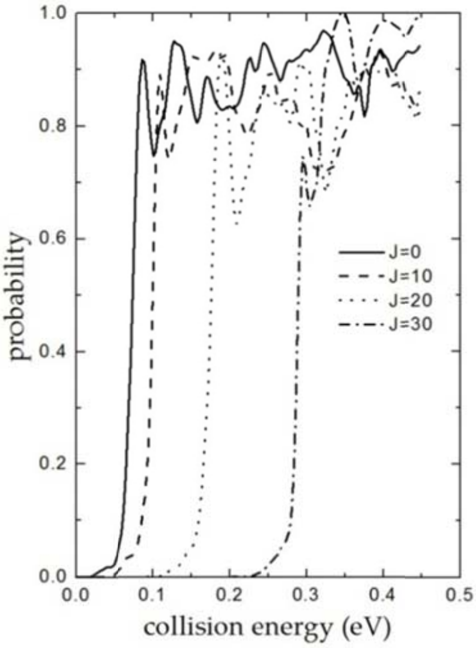

Figure 5: Total reaction probabilities as a function of collision energies for selected values of total angular momentum calculated using the centrifugal sudden approximation for the N+H_2(v=0,j=0). Solid line: J=0. Dash line: J=10. Dot line: J=20. Dash Dot line: J=30.

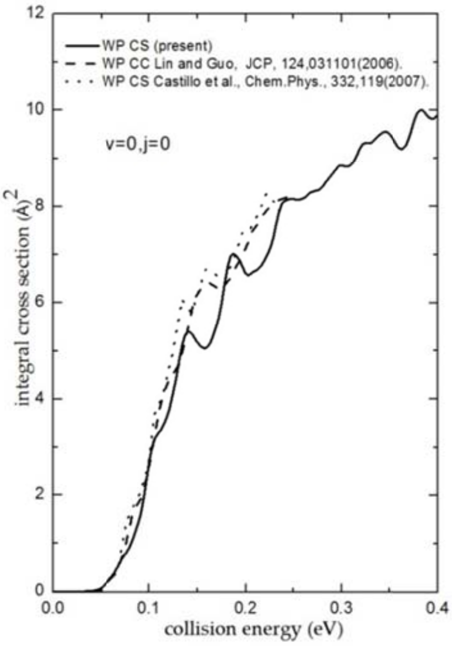

Figure 6: Integral cross-sections as a function of collision energy.

Summary

In this work, time dependent real wave packet method is implemented on a recently developed potential energy surface by Yang et al. [14]. On this surface first accurate total and state-to-state reaction probabilities, product vibrational and rotational distribution are calculated at total angular momentum *J*=0. The effects of initial rotation and vibration on the reactivity are also investigated. Initial state integral cross sections have been calculated using Centrifugal Sudden Approximation and compared with the data available in the literature. It is found that the initial rotation and vibration has a big effect on the reactivity at least for the state-to-state reaction probabilities at *J*=0. The calculated Integral cross sections by using CS approximation are quite good agreement with the available CC results in the literature especially in the low collision energy range.

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