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Quantum Mechanics Rate Constant for the N+ND Reaction[†]

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We present nonadiabatic quantum dynamical calculations on the two coupled potential energy surfaces ($1^2A'$ and $2^2A'$) [J. Theor. Comput. Chem. **8**, 849 (2009)] for the reaction. Initial state-resolved reaction probabilities and cross sections for the $N+ND\rightarrow N_2+D$ reaction and $N'+ND\rightarrow N+N'D$ reaction for collision energies of 5 meV to 1.0 eV are determined, respectively. It is found that the $N+ND\rightarrow N_2+D$ reaction is dominated in the $N+ND$ reaction. In addition, we obtained the rate constants for the $N+ND\rightarrow N_2+D$ reaction which demand further experimental investigations.

Key words: Nonadiabatic quantum dynamical calculation, $N+ND\rightarrow N_2+D$ reaction, Rate constant

I. INTRODUCTION

The N_xH_y systems have become increasing attractive because of their important role in combustion chemistry and astrochemistry. It is well established that the NH radical is an important intermediary species in combustions, particularly those concerning the reduction of the NO pollutant [1–4] and is relevant for the understanding of noncatalytic radical mechanisms leading to ammonia formation [5]. Moreover, the $NH+N$ exothermic reaction may be considered as one of the simplest ways to produce N_2 in astrochemical models [6, 7].

Despite of its importance, there has been few experimental study of the $N+NH\rightarrow N_2+H$ reaction. The only experimental measurement is reported by Hack *et al.* using a quasi-static laser flash-photolysis cell method at 298 K [8]. For other temperatures, only crude estimates have been presented based on indirect means [9–13]. Furthermore, experimental estimate for the N_2H lifetime is about 0.1 ms, while the theoretical studies of HN_2 unimolecular decay predict a much shorter value of 1–10 μ s [14, 15]. It has been suspected that the significant discrepancy between the theoretical and experimental estimates of the N_2H lifetime is likely due to the neglect of nonadiabatic effects. However, Yang *et al.* reported that nonadiabatic effects for the $N+NH\rightarrow N_2+H$ reaction is negligible [16]. On the theoretical side, Varandas and co-workers have constructed several potential energy surfaces (PESs) from high quality *ab initio* calculations for the N_2H system [17, 18].

Based on their PESs, they calculated the rate constants over a large temperature range using the method of quasi-classical trajectory and capture theory [18]. In addition, Frankcombe and Nyman [19] reported their calculated thermal rate constants over the temperature range 2–300 K using the adiabatic capture centrifugal sudden approximation (ACCSA). Recently, Yang *et al.* calculated thermal rate constants cover temperatures between 10 and 4000 K using a time-dependent quantum wavepacket (TDQW) method [20]. However, all the theoretical calculated rate constants mentioned above are larger than experimental measurement at room temperature. As far as we know, there is no reported experimental and theoretical rate constants for the $N+ND\rightarrow N_2+D$ reaction. In this work we perform the nonadiabatic quantum dynamics for the title reaction to obtain the rate constants.

II. THEORY

A. Potential energy surfaces

Based on multi-reference configuration interaction (MRCI) energies, Varandas and co-workers have reported the first accurate realistic global PES for the ground electronic state $1^2A'$ of the title system [17]. Subsequently, this PES has been refined by fitting additional MRCI energies in the $N\cdots NH$ channel, yielding a PES hereinafter referred to as DMBE (double many-body expansion) 1v-II [18]. In addition, they constructed the diabatic potential energy surfaces (PESs) denoted as DMBE 2v-II [6] using further detailed MRCI/aug-cc-pVTZ calculations for the coupled $1^2A'/2^2A'$ states of the title system.

In the present work, we will perform nonadiabatic quantum dynamical calculations employing the DMBE

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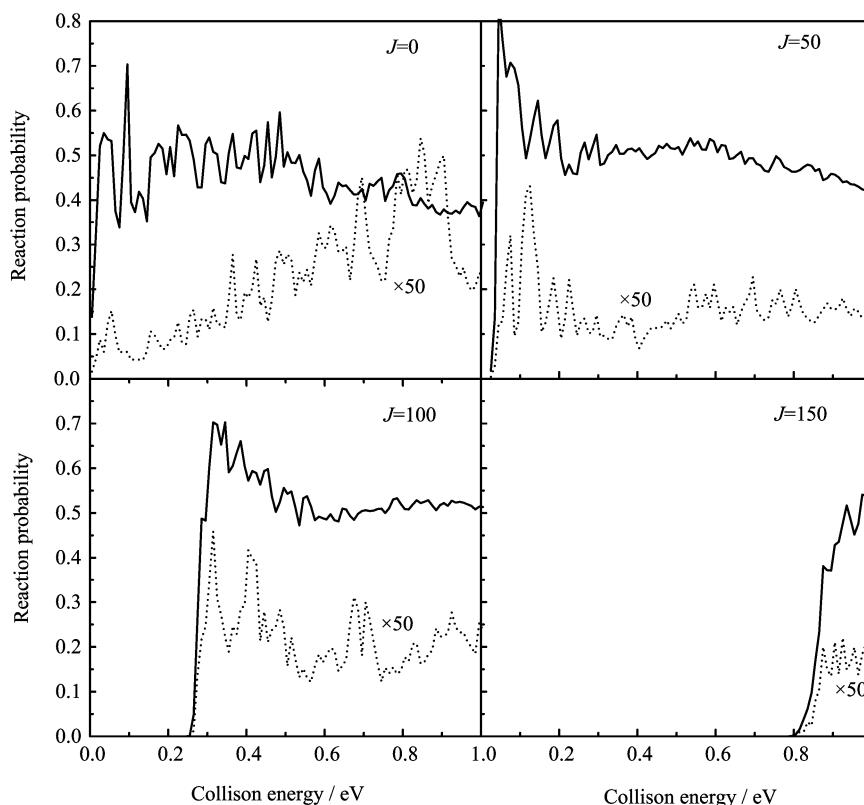


FIG. 1 Energy dependence of the initial state ($v_i=0, j_i=0$)-specified reaction probabilities for the $N+ND \rightarrow N_2+D$ reaction and $N'+ND \rightarrow N+N'D$ reaction for the total angular momentum $J=0, 50, 100$, and 150 , respectively. The solid lines and dashed lines are the results for the $N+ND \rightarrow N_2+D$ reaction and $N'+ND \rightarrow N+N'D$ reaction, respectively.

$2v$ -II PES. The overall reaction is exothermic by 6.36 eV, implying a very strong tendency for any N_2H formed to go on to produce the N_2+H products. There is a strongly bond complex (N_2H) with a deep well and a small barrier with height of 0.46 eV in the minimum energy path (the deep well is about 6.2 eV relative to the reactant $N+NH$ asymptote and the small barrier is relative to the global minimum). Note that the barrier for $H-N_2$ isomerization is about 1.95 eV relative to the global minimum.

III. RESULTS AND DISCUSSION

Figure 1 shows the Coriolis-coupled (CC) reaction probabilities for the $N+ND \rightarrow N_2+D$ reaction and $N'+ND \rightarrow N+N'D$ reaction for the total angular momentum $J=0, 50, 100$, and 150 , respectively. The nonadiabatic quantum dynamical calculations are the same as those used in Refs.[21–27]. It is clear that the probabilities of both channels are dominated by a resonance structure which is mainly due to the deep well somewhere late in the entrance channel before products formation. For clarity, the results for the $N'+ND \rightarrow N+N'D$ reaction shown in Fig.5 are multiplied by 50. Even so, the probabilities of $N'+ND \rightarrow N+N'D$

reaction are still less than those of $N+ND \rightarrow N_2+D$ reaction. That is to say, the $N+ND \rightarrow N_2+D$ reaction is dominated in the $N+ND$ system. It is easy to understand from the N_2H PES in which the $N+ND$ product channel is very high and hard to access. In addition, the probabilities of $N+ND \rightarrow N_2+D$ reaction for all the total angular momentum generally decrease with increasing initial collision energy due to a deep well in the PES, while the probabilities of $N'+ND \rightarrow N+N'D$ reaction for $J=0$ show increase trend but will not influence the trend of integral cross sections (see below).

Figure 2 displays the calculated integral cross sections (ICSs) for the $N+ND \rightarrow N_2+D$ reaction and $N'+ND \rightarrow N+N'D$ reaction, along with the sum of them. For clarity, the results for the $N'+ND \rightarrow N+N'D$ reaction shown in Fig.2 are multiplied by 50. Even so, the ICSs of $N'+ND \rightarrow N+N'D$ reaction are still less than those of $N+ND \rightarrow N_2+D$ reaction which is in accordance with Fig.1. The ICSs for both the N_2+D channel and $N+N'D$ channel generally decrease with increasing initial collision energy due to a deep well in the PES in the entrance channel before products formation. Comparing the total ICSs with the $N+ND \rightarrow N_2+D$ reaction ICSs, there is very little difference between the total and $N+ND \rightarrow N_2+D$ reaction ICSs, suggesting a very significant role of the N_2+D channel for the $N+ND$ reaction

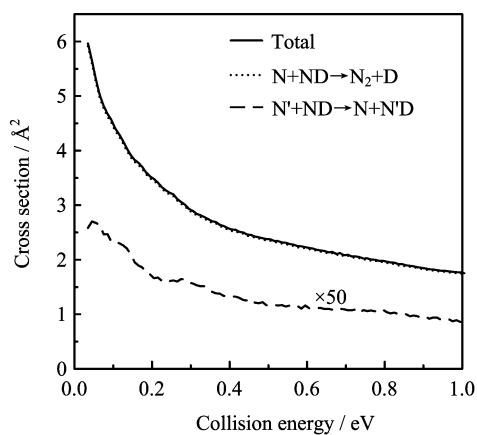


FIG. 2 The initial state ($v_i=0$, $j_i=0$)-specified ICS for $N+ND\rightarrow N_2+D$ reaction and $N'+ND\rightarrow N+N'D$ reaction. The dotted, dashed and solid lines are the results obtained from nonadiabatic calculations for $N+ND\rightarrow N_2+D$ reaction and $N'+ND\rightarrow N+N'D$ reaction and the sum over the two channels, respectively.

for collision energy up to 1.0 eV.

The CC and CS (centrifugal sudden approximation) calculated initial state specified rate constants for the $N+ND\rightarrow N_2+D$ reaction are shown in Fig.3. Both the CC and CS rate constants increase monotonically as the temperature increases and then tend to level off above 2000 K which is similar to the $N+NH\rightarrow N_2+H$ reaction. As can be seen, neglecting Coriolis coupling will underestimate the rate constant which accords with Chu *et al.*'s conclusion that neglecting Coriolis coupling for a complex-forming mechanism with a deep well will underestimate the ICS [28]. At very low temperatures (below 100 K), the differences between the CC and CS rate constants are very small, but as the temperature increases, the differences become larger and then remain constant above 2000 K. Therefore, Coriolis coupling effect plays an important role for the $N+ND\rightarrow N_2+D$ reaction especially in the high collision energy range. To the best of our knowledge, there is no reported experimental rate constants for the $N+ND\rightarrow N_2+D$ reaction, implying that our calculated rate constants demand further confirmation by experimental investigations.

IV. CONCLUSION

We have performed the nonadiabatic quantum dynamical calculations for the $N+ND\rightarrow N_2+D$ reaction and $N'+ND\rightarrow N+N'D$ reaction. Both reaction probabilities and integral cross sections for the $N+ND\rightarrow N_2+D$ reaction and $N'+ND\rightarrow N+N'D$ reaction have been presented for collision energies from 5 meV to 1.0 eV. It turns out that the $N+ND\rightarrow N_2+D$ reaction is dominated in the $N+ND$ system. In addition, we obtained the rate constants for the $N+ND\rightarrow N_2+D$ reaction which demand further experimental investigations.

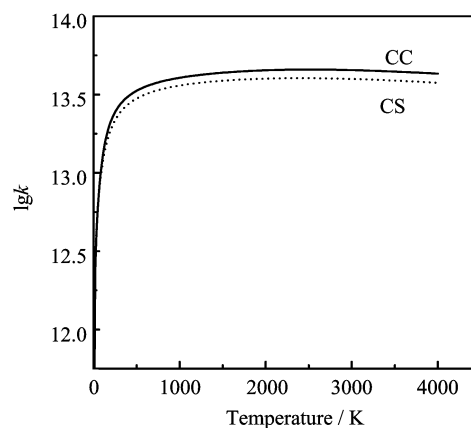


FIG. 3 Initial state-selected rate constants for the $N+ND(v_0=0, j_0=0)\rightarrow N_2+D$ reaction from the CC and CS calculations.

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