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Adiabatic wavepacket dynamics study of the N + NH → N_2 + H reaction on the ground-state potential energy surface

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ABSTRACT

Quantum dynamics calculations are reported for N + NH → N_2 + H reaction on the lowest doublet state potential energy surface of HN_2 [26]. The calculations have been performed for $J = 0$ using the time-dependent real wavepacket approach [29]. Reaction probabilities for total energies between 0.1 and 0.7 eV are presented, as well as vibrational and rotational state distributions for products at three total energies. Integral cross sections obtained by the J-shifting method, and the rate constant as a function of temperature are also given.

1. Introduction

N_xH_y systems have attracted increasing attention in recent years because of their important functions in combustion chemistry and astrochemistry. Specifically, the NH radical is important in the noncatalytic radical mechanism for ammonia formation [1], whereas N_2H is a well-known intermediate of NO_x pollutant combustion reduction [2–5]. Particularly, the reaction NH + N → N_2 + H (1) is crucial in the combustion of nitrogen-containing species [6,7], such as ammonia [8,9] and hydrazine [10,11]. Despite their importance, N_xH_y systems have rarely been the subject of measurement studies. Hack et al. [12] used a quasi-static laser flash photolysis cell at room temperature ($T = 298$ K) to directly measure the rate constant of N_2H system. Only crude estimates obtained by indirect means have been suggested for other temperatures [7,10,11,13]. Theoretically, Frankcombe et al. [14] performed adiabatic capture centrifugal sudden approximation (ACCSA) to study the kinetics of the title reaction and obtained thermal rate constants in the temperature range of 2–300 K.

Further theoretical studies have been recently performed to calculate the lifetime of N_2H. The results obtained using theoretical methods revealed that N_2H should be metastable with a very short lifetime [15–17]. However, previous studies [6,18,19] using chemical kinetic models of the thermal De-NO_x process assume that N_2H has a long lifetime. Mota et al. [20] proposed that the significant discrepancies that persist between the theoretical and experimental estimates are probably due to the neglect of nonadiabatic effects. However, our earlier study [21] implied that the nonadiabatic effects for the initial state of NH ($v = 0, j = 0$) could be neglected for collision energies up to 1.0 eV.

Considerable theoretical studies have concentrated on the potential energy surfaces (PESs) of the title system. These studies are listed in Ref. [20]. Varandas et al. reported [17] the first accurate and realistic global PES for the ground electronic state of the title system based on multi-reference configuration interaction (MRCI) energies and modeled this PES based on double many-body expansion (DMBE) theory [22,23]. Specifically, they calculated 900 MRCI geometries using the aug-cc-pVQZ basis set of Dunning [24,25] and the full valence complete active space wave function as reference. Subsequently, this PES was refined by fitting additional MRCI energies in the N. . .NH channel [26]. This refinement process yielded a PES hereafter referred to as DMBE 1v–II. Moreover, further detailed MRCI/aug-cc-pV*T*Z calculations were performed by the Coimbra Group for the coupled $1^2A'/2^2A'$ states of the title system to investigate the excited states and nonadiabatic effects [20,27]. The energies obtained were diabatized to yield the matrix elements of a 2 × 2 diabatic potential matrix. Finally, these elements were modeled to generate a global (diabatic) multi-sheeted DMBE PES [28], hereafter denoted as DMBE 2v-II. Both the above PESs have been utilized in dynamic and kinetic calculations, including the ACCSA studies by Franckombe and Nyman [14], which employed DMBE 1v-II. Specifically, adiabatic calculations using the quasi-classical trajectory (QCT) method have been carried out on the lowest doublet state of the DMBE 1v-II and DMBE 2v-II PESs [27,28]. These calculations yielded similar results. Thus, both PESs should have a similar degree of reliability. In addition, both are recommended for use in more accurate dynamic calculations. Accordingly, the present study aims to apply the adiabatic time-dependent wavepacket approach on DMBE 1v-II to obtain accurate information and to estimate quantum effects. We will concentrate on DMBE 1v-II PES. Nevertheless, rigorous close-coupling calculations were performed [21] on DMBE 2v-II PES to elucidate the function of the non-adiabatic effects in the title reaction.

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2. Potential energy surface

The PES utilized in the present study was DMBE 1v-II, which has been previously described in detail [17,27]. DMBE 1v-II is shown in Figure 1, which shows the corresponding minimum energy path for the reaction $N + NH \rightarrow N_2 + H$. This path is formed by searching for the minimum energy along a line that swings from the N + NH to the $H + N_2$ valleys. The zero point of the potential energy was taken at the N—H—H dissociation limits. The reaction occurs without a potential barrier in the entrance channel, with only a very small barrier on the exit channel; thus well below the energy of the reactants. Moreover, the shape of such a minimum energy profile for reaction typifies the one expected to yield capture-type dynamics, which explains the use of quantal (such as ACCSA [14]) and classical [26] methods. A comparison with such results will be reported in the following section.

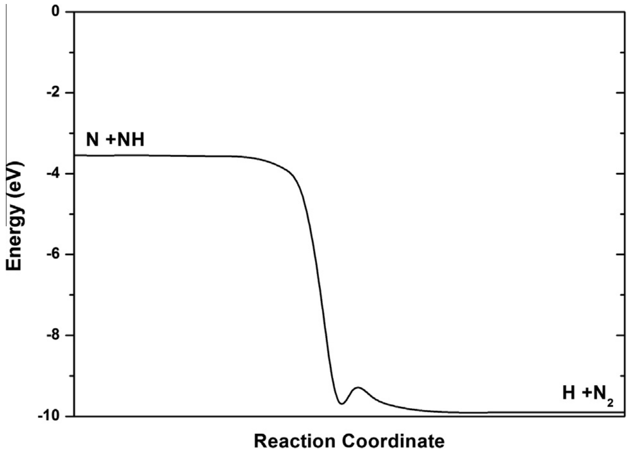

Figure 1. Minimum energy paths for the reaction $N + NH \rightarrow N_2 + H$ on DMBE 1v-II. The zero point of potential energy was measured at the N—H—H dissociation limits.

3. Results and discussion

The method employed for the calculations is the time-dependent real wavepacket (TDRW) approach by Gray and Balint-Kurti [29] in product coordinates to compute state-to-state reaction probabilities. The method has been well documented in literature [30–33]. All parameters used in the calculation are listed in Table 1. The total energy (translational energy + initial state energy) is in the range of 0.1–0.7 eV. Several calculations with varied initial translational energies were performed to cover this energy range (Table 1). In all calculations, the reactant diatom NH was maintained in the ground ro-vibrational state.

Figure 2 shows the reaction probabilities on the ground-state PES yielding N_2+H products. The overall reaction is exothermic by 611 kJ/mol (6.33 eV, Figure 1) [14]. Thus, a large amount of energy is expected to be rearranged, implying a very strong tendency for the newly formed N_2 to be excited. Figure 2 shows the probability of reaction jumps to reach ~1 even for near-zero collision energies, which then decreases to ~0.9 for the entire energy range. Moreover, the reaction probabilities show hardly any structure, although several broad peaks were present. We also show the result of Yang et al. [21] using the time-dependent wavepacket method [34] on the lower sheet of DMBE 2v-II PES for comparison. The general features for the two reaction probabilities are similar. However, the reaction probability on DMBE 2v-II has more structure and is smaller in magnitude, which is possibly because of the differences in PESs.

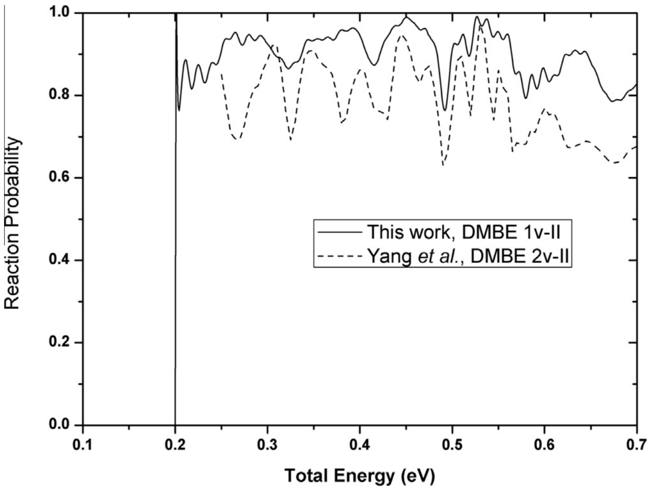

Figure 2. Reaction probabilities vs. total energy in eV for the $N_2 + H$ product arrangement channel.

Table 1
Grids and initial details in the calculations. All quantities are in atomic units unless stated otherwise.

Variable	
Scattering coordinate (R) range	0–16
Number of grid points in R	499
Internal coordinate (r) range	0–16
Number of grid points in r	499
Number of angular grid points	100
Absorption region length in R (r)	5 (5)
Absorption strength in R (r)	0.5 (0.5)
Center of initial wavepacket (R_0)	8
Width of the wavepacket	8
Smoothing of the wavepacket	0.2
Initial translational energy (eV)	0.1, 0.3, 0.4
Analysis line R_∞	10

Figure 3a compares the vibrational distributions for N_2 product from the TDRW and QCT calculations [28] at a total energy of 0.287 eV (2 kcal/mol collision energy). In both cases, N_2 is in highly excited vibrational state with inverted vibrational distribution. Their shapes are similar, with a peak near $v' = 16$. Meanwhile, three sharp peaks were observed for TDRW with a pronounced peak at $v' = 23$. Figure 3b shows the corresponding total rotational distribution of N_2 for both methods. The features show significant differences at the QCT and TDRW/$J = 0$ levels. A non-Boltzmann distribution is predicted for the QCT results, with a maximum peak at $j' = 40$. By contrast, the distribution relative to the TDRW/$J = 0$ results appear similar to a Boltzmann distribution but highly structured and with the highest rotational states below 40. The extent to which excited *rotational* states contribute to promote agreement with the QCT results remains to be determined. Tentatively, we could at least partially attribute the disagreement to lack of thermalization of the wavepacket calculations.

Figure 3 also shows the vibrational and rotational distributions of newly formed N_2 at three total energies. Figure 3 shows that both vibrational and rotational distributions tend to populate higher excited states with increasing collision energy; thus, higher vibrational states become more favorable. In other words, the reaction exoergicity can be easily converted into the vibrational degree of freedom of the diatomic product.

State-to-state reaction probabilities for several selected vibrational states are shown in Figure 4. The curves clearly show a considerable increase in structure for the higher vibrational states of N_2, whereas the probabilities are significantly flatter for the lower