

REGULAR ARTICLE

Theoretical calculation of vector correlations for the reaction

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Abstract: The stereodynamics of the reaction $\text{H}(^2\text{S}) + \text{NH} (\nu = 0, 1, 2, 3; j = 0) \rightarrow \text{N}(^4\text{S}) + \text{H}_2$ are studied using the quasi-classical trajectory method on a double many-body expansion potential energy surface to understand the alignment and orientation of the product molecules in the collision energy range of 2–20 kcal·mol⁻¹. The vibrational-rotational quantum number of the NH molecules is specifically investigated for $\nu = 0, 1, 2$, and 3 and $j = 0$. The $P(\theta_r), P(\phi_r), P(\theta_r, \phi_r)$, differential cross section [DCS; $(2\pi/\sigma)(d\sigma_{00}/d\omega_t)$], and average rotational alignment factor $\langle P_2(\cos \theta_r) \rangle$ are calculated. The stereodynamics results indicate that the reagent vibrational quantum number and initial collision energy significantly affect the distributions of the $k-j', k-k'-j'$ and $k-k'$ vector correlations along with $\langle P_2(\cos \theta_r) \rangle$. In addition, while DCS is extremely sensitive to the collision energy, it is not significantly affected by the vibrational excitation of the reagents.

Keyword: quasi-classical trajectory method, stereodynamics, potential energy surface, vector correlation

1. Introduction

Reactions between nitrogen and hydrogen atoms have attracted the attention of experimental and theoretical chemists for the past 30 years. With the development of molecular beam and polarized laser light techniques, [1,2] elementary chemical reactions can now be easily studied. Much of the information about an elementary chemical reaction is summarized by its excitation function or rate constant. Morley[3] studied NO formation

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from nitrogen compounds in hydrogen flame using laser fluorescence and determined the rate constant for the reaction between NH and H atoms at 1790–2200 K. In 1990, Koshi and Yoshimura[4] measured the rate constant for the reaction between $N(^4S)$ and H_2 at high temperature (1950–2850 K). In addition, the rate constant for the reaction $N + H_2 \rightarrow NH + H$ was reported as $1.60 \times 10^{14} \exp(-12650/T) (\pm 35\%) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ from 1950 to 2850 K.[5] In 2005, Adam et al.[6] obtained a rate constant of $k = (1.9 \pm 0.5) \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the reaction $NH + H \rightarrow N + H_2$ using quasi-static laser-flash photolysis at room temperature.

Poveda and Varandas [7] theoretically derived the repulsive double many-body expansion[8] (DMBE) potential energy surface (PES) for the triatomic fragment of the $NH_2(4A')$ reactive system at the MRCI/aug-cc-pVQZ level of theory.[9,10] For both the forward reaction $N(^4S) + H_2 \rightarrow H(^2S) + NH$ and reverse reaction $H(^2S) + NH \rightarrow N(^4S) + H_2$, their calculations agreed with the experimental results and the best-available theoretical estimates. Consequently, many dynamic studies of forward and reverse reactions followed [11–15] this successful derivation of the DMBE PES using high-level ab initio calculations. For example, Zhang et al.[11] investigated the effect of isotope substitution on the stereodynamics of forward reactions at a collision energy of $40 \text{ kcal} \cdot \text{mol}^{-1}$ and discussed the distributions $P(\theta_r)$, $P(\phi_r)$, and $P(\theta_r, \phi_r)$ of the vector correlations between products and reagents. Yu et al.[12] studied the rotational excitation and collision energy of the forward reaction $N(^4S) + H_2 (v=0, j=0, 2, 5, 10) \rightarrow NH(X^3\Sigma^-) + H$ using the quasi-classical trajectory (QCT) method. Using the same method, Xia et al.[13] investigated the effects of isotope substitution and collision energy on the stereodynamics of the forward reaction. Yu et al.[14] discussed the product polarization of the forward reaction $N(^4S) + H_2 (v=0-3, j=0) \rightarrow NH(X^3\Sigma^-) + H$ for collision energies from 25 to $140 \text{ kcal} \cdot \text{mol}^{-1}$ and calculated four polarization-dependent differential cross sections (PDDCSs) along with the distributions $P(\theta_r)$, $P(\phi_r)$, $P(\theta_r, \phi_r)$ and $\langle P_2(\cos \theta_r) \rangle$ for the rotational ground state and vibrational excited states of the reagent. For

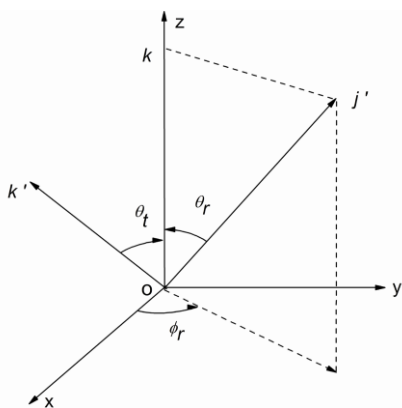


Figure 1: Center-of-mass coordinate system that describes the correlation between k , k' , and j' .