



Reactive scattering of an electronically-excited nitrogen atom with H₂ and its isotopic variants: N(²D) + H₂/D₂/T₂



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ABSTRACT

Total reaction probabilities, integral cross sections and total rate constants of the N(²D) + H₂ reaction and its isotopic variants were calculated using a time-dependent quantum wave packet method with a centrifugal sudden approximation on the latest reported global potential energy surface. The effect of rotational excitation of the diatoms and its projection quantum number on the behaviour of reaction probabilities was studied. Reaction probabilities were calculated using a flux wave packet method. The results indicate that the reaction kinetics are affected by intermolecular isotope and collision energies.

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1. Introduction

Ground-state nitrogen N(⁴S) is inertial, and therefore, has a long lifetime and it is only slightly reactive (for symmetry and thermodynamical reasons). However, the title reaction of the first excited (²D) state of nitrogen, N(²D) + H₂ → NH(³Σ⁻) + H, makes the excited nitrogen atom very reactive. Therefore, excited nitrogen plays a significant role in the chemistry of planetary atmospheres, combustion chemistry, interstellar chemistry and plasma chemistry [1]. Due to the reactive behaviour of the excited-state of the N(²D) atom, significant attention has been directed towards the atom in this state and its collisions with H₂ in recent experimental and theoretical studies [2–7]. The atmosphere of Saturn's largest moon, Titan, is mainly composed of molecular nitrogen, in addition to 2–5% methane [8,9] and some reaction products of N(²D) with simple hydrocarbons [10–12].

This chemical reaction has been studied both experimentally and theoretically [1–34]. The early experimental work of Fell et al. [13] monitored the concentrations of N(²D_{3/2}) and N(²D_{5/2}) with electron spin resonance. Afterwards, in 1991, Dodd et al. [14] studied vibrational distributions of NH and produced time-resolved infrared emission measurements. In another study, Suzuki et al. [15] obtained the temperature-dependent rate constants of the reactions of N(²D) with H₂ and D₂. Umemoto et al. [16–18] produced the excited nitrogen atom N(²D) by photodissociation of NO, and obtained the ratio of the vibrational levels of the NH molecule using an intense laser pulse at 275.2 nm in laser-induced fluorescence. In 1999, Alagia et al. [19] first performed a

reactive scattering study of nitrogen atoms and obtained the angular and velocity distributions of the ND product from the reaction N(²D) + D₂ using a crossed molecular beam. The obtained results were compared with early quasiclassical trajectory (QCT) calculations, which were theoretical, and the experimental and theoretical results were found to be similar. In 2001, Balucani et al. [20] performed further experimental and theoretical work. They obtained experimental values for the angular and velocity distributions of the ND product from crossed molecular beam experiments, and reproduced the centre-of-mass product angular and translational energy distributions. In the theoretical part of their study, the (QCT) method recently developed by Pederson et al. [21] was used.

Kobayashi and co-workers [22] theoretically developed an *ab initio* potential energy surface (PES) for the ground-state NH₂ system, based on first-order configuration interaction (FOCI) calculations. For N(²D) + H₂/D₂ reactions, Pederson et al. [21] calculated reaction kinetics and product distributions on the ground (PES) by using (QCT) calculations based on the kernel Hilbert space interpolation method. They compared their results with calculations for the lower level of the first FOCI surface and found that the only true reaction path for their surface was the FOCI surface. Again, using this PES, Honvault and Launay [23] obtained reaction kinetics and product distributions using the hyperspherical coordinate quantum mechanical time-independent (QM-TI) method for total angular momentum quantum numbers, *J*, up to 26. Takayanagi and co-workers [24] computed two-dimensional PESs for the N + H₂ reaction using the *ab initio* multireference configuration interaction method. The calculations showed that not only the

lowest doublet surface but also the second lowest doublet surface contributed to the reaction dynamics of $N(^2D) + H_2$. Rackham et al. [25] determined the exact quantum mechanical integral cross section with coupled channel capture theory and found that their result supported the results recently reported by Honvault Launay and the experimental evaluation of Umemoto et al. [17]. Ho et al. [26] calculated the differential cross sections (DCSs) and rate constants of the vibrational and rotational distributions of the $N(^2D) + H_2(X^1\Sigma_g^+)$ reaction on the ground-state PES, which they developed themselves. For the same PES, Banares and co-workers [27] calculated the integral cross sections and thermal rate constants for $N + H_2$ and its isotopic variants, which used the QCT method and statistical quantum-mechanical model methods. For the same PES, Castillo et al. [28] computed total initial state-selected and final state-resolved reaction probabilities and product rotational distributions for total angular momentum $J = 0$ using split operator and QCT methodologies. Due to the high reactivity of $N(^2D)$, Pederson and co-workers [29] presented a global PES for the second lowest electronic state ($1^2A'$) depending on an interpolation technique known as reproducing the kernel Hilbert space (RKHS), and Akpınar et al. [30] calculated the reaction dynamics of $N(^2D) + H_2$ using the QCT method on this PES. In addition to theoretical studies, several dynamical studies have also been recently reported [31–34].

Yang et al. [35] constructed a new analytical potential energy surface (APES) for the $N(^2D) + H_2(X^1\Sigma_g^+) \rightarrow NH(X^3\Sigma^-) + H(^2S)$ reaction. In this reaction, the N atom is in the excited [36] D state for the $N + H_2$ asymptote, but in the ground state for the $NH + H$ asymptote; consequently, the same atom has different states in different dissociative asymptotes [35]. This new potential surface is represented with a many-body expansion and a new switch function that contains all of the interatomic distances of the system. It is accurate in the range of small internuclear distances, which can ensure reliable potential energies for each part of the dynamics structure [35].

In our study, the real wave packet (RWP) method was used to study $N + H_2(D_2/T_2)$ reactions, combined with a flux method and a centrifugal sudden (CS) approximation for $J > 0$ states. The rest of this paper is organised as follows. The theory is outlined in Section 2 and the results are discussed in Section 3.

2. Method

In the present study, the RWP method of Gray and Balint-Kurti [37] using the Chebyshev operator propagator method was used to calculate the reaction dynamics of $N(^2D) + H_2$ and its isotopic variants on the PES provided by Yang et al. [35]. To study $N(^2D) + H_2/D_2/T_2$, a body-fixed (BF) frame representation was adopted with reactant Jacobi coordinates [38], identified as $(R_\alpha, r_\alpha, \gamma_\alpha, K_\alpha)$. As in previous work [32], the Hamiltonian for $J = 0$ was expressed in the product Jacobi coordinates, $(R_\alpha, r_\alpha, \gamma_\alpha)$. Here R_α is the distance from the N atom to the centre of mass of the $H_2/D_2/T_2$ molecule, r is the vibrational coordinate of the diatomics and, γ is the angle between R and the r vectors [39].

In the reactant Jacobi coordinates $(R_\alpha, r_\alpha, \gamma_\alpha)$, the Hamiltonian for a given total angular momentum J can be written as

$$\hat{H} = -\frac{\hbar^2}{2\mu_{R_\alpha}} \frac{\partial^2}{\partial R_\alpha^2} - \frac{\hbar^2}{2\mu_{r_\alpha}} \frac{\partial^2}{\partial r_\alpha^2} + \frac{(J-j)^2}{2\mu_{R_\alpha} R_\alpha^2} + \frac{j^2}{2\mu_{r_\alpha} r_\alpha^2} + V(R_\alpha, r_\alpha, \gamma_\alpha) \quad (1)$$

where μ_{R_α} indicates the reduced masses of N and H_2 and, μ_{r_α} indicates the reduced mass of H_2 . J is the total angular momentum operator, j is the rotational angular momentum operator of H_2 and $V(R_\alpha, r_\alpha, \gamma_\alpha)$ is the PES of the $N-H_2$ system described previously [35]. With a spherical harmonic basis, $y_{jK}(\theta_\alpha)$ is used for the angular

degree of freedom, which as a finite basis representation (FBR) time-dependent wave packet can be given as [38,40–43].

$$\psi^{JM_\varepsilon}(R_\alpha, r_\alpha, t) = \sum_{K_\alpha} D_{MK_\alpha}^{J\varepsilon}(\Omega_\alpha) \psi_\alpha(t, R_\alpha, r_\alpha, \theta_\alpha^{K_\alpha}; K_\alpha) \quad (2)$$

where $D_{MK_\alpha}^{J\varepsilon}(\Omega_\alpha)$ is the normalised rotation matrix

$$D_{MK_\alpha}^{J\varepsilon}(\Omega_\alpha) = (1 + \delta_{K_\alpha 0})^{-1/2} \sqrt{\frac{2J+1}{8\pi}} \left[D_{MK_\alpha}^{J*}(\Omega_\alpha) + \varepsilon(-1)^{J+K_\alpha} D_{M-K_\alpha}^{J*}(\Omega_\alpha) \right] \quad (3)$$

Here $\varepsilon = (-1)^{l+j}$ is the parity, l is the orbital angular momentum quantum number and K is the projection of the total angular momentum J along the BF z -axis (R) [44]. In Eq. (2) $\psi_\alpha(t, R_\alpha, r_\alpha, \theta_\alpha^{K_\alpha}; \Omega_\alpha)$, which depends only on three internal coordinates of the system and the projection of the total angular momentum K_α on the BF z -axis can be written as

$$\psi_\alpha(t, R_\alpha, r_\alpha, \theta_\alpha^{K_\alpha}; K_\alpha) = \sum_{n,m,j} F_{nmj}^{K_\alpha}(t) u_n(R_\alpha) \phi_m(r_\alpha) y_{jK_\alpha}(\theta_\alpha) \quad (4)$$

Here n and m are the translational basis labels, $u_n(R_\alpha)$ and $\phi_m(r_\alpha)$ are the translational basis functions for R and r , respectively and $y_{jK_\alpha} = \sqrt{[(2j+1)/4\pi]} d_{jK_\alpha 0}^j$ indicates the spherical harmonics. $d_{\Omega_\alpha \Omega_\nu}^j$ is a reduced Wigner rotational matrix [45] with $\Omega_\nu = 0$.

In Eq. (1), the Coriolis coupling term, which is off-diagonal in K states in the BF representation is given by

$$\frac{\hbar^2}{2\mu_r R^2} \langle Y_{jK}^{JM_\varepsilon} | (J-j)^2 | Y_{jK'}^{JM_\varepsilon} \rangle \delta_{nm'} \delta_{\nu\nu'} \quad (5)$$

$$= \frac{\hbar^2}{2\mu_r R^2} \delta_{j'j} \left\{ [J(J+1) + j(j+1) - 2K^2] \delta_{KK'} - \lambda_{jK}^+ \lambda_{jK}^+ (1 + \delta_{K0})^{1/2} \delta_{K+1,K'} - \lambda_{jK}^- \lambda_{jK}^- (1 + \delta_{K1})^{1/2} \delta_{K-1,K'} \right\}$$

and the quantity λ is denoted as

$$\lambda_{jK}^\pm = \sqrt{J(J+1) - K(K \pm 1)} \quad (6)$$

$$\lambda_{jK}^\pm = \sqrt{j(j+1) - K(K \pm 1)} \quad (7)$$

Eqs. (6) and (7) define the so-called Coriolis coupling terms [46,47]. In these equations, different K states in the wave function couple together. For this reason, more basis functions are needed to store the exact information about the wave function. Increasing the number of grid points in the angular part requires more computer memory. Hence, here, for computing the reaction probabilities for $J > 0$, the (CS) approximation was used. In the CS approximation, these off-diagonal elements are ignored, which considerably decreases the size of the Hamiltonian matrix [48]

$$\hat{H} = -\frac{\hbar^2}{2\mu_{R_\alpha}} \frac{\partial^2}{\partial R_\alpha^2} - \frac{\hbar^2}{2\mu_{r_\alpha}} \frac{\partial^2}{\partial r_\alpha^2} + \frac{\hbar^2}{2} \left(\frac{1}{2\mu_{R_\alpha} R_\alpha^2} + \frac{1}{2\mu_{r_\alpha} r_\alpha^2} \right) j^2 + \frac{1}{2\mu_{R_\alpha} R_\alpha^2} \times \{J(J+1) - 2K^2\} + V(R_\alpha, r_\alpha, \gamma_\alpha) \quad (8)$$

The reactant wave packet is set up in the reactant Jacobi coordinates, $\psi(R_\alpha, r_\alpha, \gamma_\alpha, t)$, and is then transformed to the product Jacobi coordinates, $\psi(R_\beta, r_\beta, \gamma_\beta, t)$ [38]. The reactant wave function can be written as

$$\psi(R_\alpha, r_\alpha, \gamma_\alpha, t) = e^{-ik_0(R_\alpha - R_{0,\alpha})} e^{-\beta(R_\alpha - R_{0,\alpha})} \times \frac{\sin[\alpha(R_\alpha - R_{0,\alpha})]}{R_\alpha - R_{0,\alpha}} \varphi_{\nu,j}(r_\alpha) P_j(\cos \gamma_\alpha) \quad (9)$$

where $\varphi_{\nu,j}(r_\alpha)$ indicates the vibrational components and $P_j(\cos \gamma_\alpha)$ indicates the rotational components of the wave function. The

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