

Non-Born–Oppenheimer State-to-State Dynamics of the $\text{N}(^2\text{D}) + \text{H}_2 \rightarrow \text{NH}(\tilde{\text{X}}^3\Sigma^-) + \text{H}$ Reaction: Influence of the Renner–Teller Coupling[†]

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This publication examines the influence of electronically nonadiabatic Renner–Teller coupling between the two lowest-lying electronic states of NH_2 on state-to-state reaction dynamics. The fully Coriolis coupled quantum mechanical calculations were carried out on the recently developed NH_2 potential energy surfaces of both the $\tilde{\text{X}}^2\text{A}''$ and $\tilde{\text{A}}^2\text{A}'$ states. It is shown that the Renner–Teller coupling has a dramatic effect on the low-lying ro-vibrational states on the excited $\tilde{\text{A}}^2\text{A}'$ potential, but its impact on the differential and integral cross sections of the $\text{N}(^2\text{D}) + \text{H}_2 \rightarrow \text{NH}(\tilde{\text{X}}^3\Sigma^-) + \text{H}$ reaction is relatively minor.

I. Introduction

The dynamics of the $\text{N}(^2\text{D}) + \text{H}_2(\tilde{\text{X}}^1\Sigma_g^+) \rightarrow \text{NH}(\tilde{\text{X}}^3\Sigma^-) + \text{H}(^2\text{S})$ reaction has served as a prototype of insertion reactions, which have attracted much recent interest.^{1–4} The reaction is also of practical importance in atmospheric and combustion chemistry.⁵ Measurements of the thermal rate constant⁶ showed an Arrhenius-type temperature dependence, indicating an intrinsic barrier along the reaction path. On the other hand, the product state distributions were found to be largely statistical,^{7–10} suggesting the existence of a reaction intermediate. Such an intermediate was recently confirmed by the nearly backward-forward symmetric angular distribution of the products observed in crossed molecular beam experiments.^{11–13}

This reaction has several unique features that distinguish it from other insertion reactions. It has a small insertion barrier (~ 0.08 eV) in the entrance channel,^{14–16} while most other insertion reactions are barrierless.⁴ The adiabatic reaction path on the ground $\tilde{\text{X}}^2\text{A}''$ state potential energy surface (PES) is dominated by a deep (~ 5.5 eV) well, which supports the metastable NH_2 intermediate. On the other hand, the reaction has a large exothermicity (~ 1.25 eV), which renders the lifetime of the reaction intermediate relatively short. In addition, the insertion pathway may compete with an abstraction pathway that has a somewhat higher barrier (~ 0.2 eV). Finally, the reaction dynamics is not entirely adiabatic as the ground $\tilde{\text{X}}^2\text{A}''$ state interacts with an excited $\tilde{\text{A}}^2\text{A}'$ state near linearity, via the so-called Renner–Teller coupling between the degenerate $^2\Pi$ pair.¹⁷ The latter feature is the focus of this study.

Because of the small number of electrons in this system, global PESs for both the ground and excited states of NH_2 have been developed for reaction dynamics studies.^{14–16,18,19} These PESs are usually not spectroscopically accurate. On the other hand, semiglobal PESs near the NH_2 equilibrium geometry have

also been constructed on the basis of either ab initio or spectroscopic information.^{20,21} Although the latter types are typically more accurate in reproducing the spectral lines,^{20–23} they are unsuitable for dynamics calculations because they do not extend to the dissociation limits. Very recently, we have reported new global PESs for both the $\tilde{\text{X}}^2\text{A}''$ and $\tilde{\text{A}}^2\text{A}'$ states of NH_2 based on large scale high-level ab initio calculations aimed at a uniformly accurate characterization of both the spectroscopy and dynamics of this important system.^{24,25} Vibrational levels on both the ground and excited states have been shown to be quite accurate on these PESs.

The dynamics of the title reaction on the ground $\tilde{\text{X}}^2\text{A}''$ state PES has been extensively investigated using both quasi-classical trajectory (QCT) and quantum mechanical (QM) methods.^{11–14,19,24,26–34} A QM treatment is needed for quantitatively accurate characterization of this reaction because of the involvement of large zero-point energies and tunneling. It is well established that the adiabatic dynamics is dominated by the insertion of the nitrogen atom into the H_2 molecule, leading to the NH_2 intermediate complex. The decay of the reaction intermediate yields a near forward–backward symmetric product angular distribution, a hot rotational distribution, and cold vibrational distribution, in good agreement with experimental data. These dynamical attributes can also be reasonably reproduced by statistical models.^{35–37} In addition, the $\text{NH} + \text{H} \rightarrow \text{H} + \text{NH}$ exchange reaction has also been studied on the same NH_2 ground and excited states.^{15,38,39}

Although the reaction proceeds largely on the ground ($\tilde{\text{X}}^2\text{A}''$) electronic state of NH_2 , nonadiabatic interactions with excited electronic states could also play a role. The most prominent candidate for the nonadiabatic dynamics is the $\tilde{\text{A}}^2\text{A}'$ state, which correlates with the same reactants as the ground $\tilde{\text{X}}^2\text{A}''$ state. However, it leads adiabatically to the excited products $\text{NH}(\tilde{\text{a}}^1\Delta) + \text{H}(^2\text{S})$, which is ~ 1.6 eV higher than the ground state products $\text{NH}(\tilde{\text{X}}^3\Sigma^-) + \text{H}(^2\text{S})$. Although it by itself does not provide a viable reaction pathway for the title reaction, the $\tilde{\text{A}}^2\text{A}'$ state forms with the $\tilde{\text{X}}^2\text{A}''$ state a degenerate $^2\Pi$ pair at collinear geometry, coupled by the so-called Renner–Teller interaction.¹⁷

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Hence, flux from the $\text{N}(\text{D}) + \text{H}_2$ channel might get mixed by the nonadiabatic coupling. Indeed, the influence of the Renner–Teller coupling has been investigated by several groups, using both a surface-hopping trajectory and wave packet approaches.^{18,40–43} These calculations, particularly the quantum dynamical studies by Petrongolo and co-workers,^{41–43} have indicated that nonadiabatic transitions due the Renner–Teller coupling could play an important role in the reaction. Since these studies were restricted to total reactivity, however, the impact of the Renner–Teller interaction on final state resolved scattering attributes is still unclear.

In this publication, we report the first state-to-state quantum nonadiabatic dynamics for the title reaction, using the new ab initio PESs for the lowest-lying electronic states of NH_2 . The extensive quantum calculations yield quantum state-resolved differential and integral cross sections, which are directly measurable experimentally. By comparing to single surface results, we explore the influence of the nonadiabatic Renner–Teller coupling on the reaction dynamics. To verify the accuracy of the PESs, we have also carried out calculations of the ro-vibronic states of the $\tilde{\text{A}}/\tilde{\text{X}}$ system of NH_2 . This paper is organized as follows. The next section (section II) outlines the theory for both spectral and dynamical calculations. The results are presented and discussed in section III. The summary is given in section IV.

II. Theory

A. Hamiltonian and Its Discretization. As the bent H–N–H molecule approaches the linear geometry, the ground $\tilde{\text{X}}^2\text{A}''$ state and the excited $\tilde{\text{A}}^2\text{A}'$ state come close to each other. At linearity, they form a degenerate pair of a $^2\Pi_u$ character. As first pointed out by Renner,⁴⁴ it is possible for the electronic angular momentum to couple with the rotational angular momentum of the polyatomic molecule, resulting in the breakdown of the Born–Oppenheimer approximation. The so-called Renner–Teller (RT) ro-vibronic interaction was first observed in the NH_2 electronic spectrum,⁴⁵ and it may impact the dynamics of reactions on the PESs.

Because of the non-Born–Oppenheimer nature of the RT coupling, the nuclear Hamiltonian is inherently approximate. Earlier reduced-dimensional models shed much light on the problem,^{46,47} but a full dimensional Hamiltonian was not introduced until 1984. The Hamiltonian proposed by Carter et al.⁴⁸ was given in internal coordinates, which is well suited for spectroscopic studies. For scattering problems, the Jacobi coordinates are more appropriate and we follow closely the pioneering work of Petrongolo.⁴⁹ Specifically, the product (H–NH) Jacobi coordinates were used, and the body-fixed (BF) frame was defined by the choosing the z -axis along the R vector (R -embedding) and the molecular plane as the x – z plane. (Note that the coordinates and definition of the BF frame are different from our previous work.²⁵) The spinless total (electronic + nuclear) Hamiltonian representing this RT system can be expressed in atomic units as⁴⁹

$$\hat{H} = -\frac{1}{2\mu_R} \frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_r} \frac{\partial^2}{\partial r^2} + \hat{T}_{\text{rot}} + \hat{H}_{\text{el}} \quad (1)$$

where the first two terms represent the kinetic energy operators associated with radial Jacobi coordinates, R (H–NH distance) and r (N–H distance) with μ_R and μ_r as the corresponding reduced masses. The last two operators, which are responsible for the RT coupling, are the rotational kinetic energy operator

and the electronic Hamiltonian (including repulsive Coulomb interactions among the three nucleus), respectively. Specifically, $\hat{T}_{\text{rot}}$ is given by

$$\hat{T}_{\text{rot}} = \hat{T}'_{\text{rot}} + \left(\frac{B+b}{\sin^2 \gamma} - B \right) (\hat{L}_z^2 - 2\hat{J}_z \hat{L}_z) \quad (2)$$

where γ is the Jacobi angle and rotational constants are given as

$$b = \frac{1}{2\mu_r r^2} \quad B = \frac{1}{2\mu_R R^2} \quad (3)$$

The $\hat{T}'_{\text{rot}}$ operator takes the usual form

$$\hat{T}'_{\text{rot}} = (B+b)\hat{J}^2 + B(\hat{J}^2 - 2\hat{J}_z^2 - \hat{J}_+ \hat{J}_- - \hat{J}_- \hat{J}_+) \quad (4)$$

with

$$\hat{J}^2 = -\frac{1}{\sin \gamma} \frac{\partial}{\partial \gamma} \sin \gamma \frac{\partial}{\partial \gamma} + \frac{\hat{J}_z^2}{\sin^2 \gamma} \quad \hat{J}_{\pm} = -\cot \gamma \hat{J}_z \pm \frac{\partial}{\partial \gamma} \quad (5)$$

Here, $\hat{J}^2$, $\hat{J}_z$, and $\hat{J}_{\pm}$ are the squared total angular momentum, projection of J onto the BF z -axis, and its corresponding raising/lowering operators. The operator $\hat{L}_z$ is the electronic angular momentum along the BF z -axis. Following Goldfield et al.⁵⁰ the x , y components of electronic angular momentum (L_x , L_y) were ignored in eq 2.

The electronic Hamiltonian provides the Born–Oppenheimer PESs and adiabatic electronic eigenfunctions of both the A'' and A' states, i.e.

$$\hat{H}_{\text{el}}|\phi''\rangle = V''(R,r,\gamma)|\phi''\rangle \quad \hat{H}_{\text{el}}|\phi'\rangle = V'(R,r,\gamma)|\phi'\rangle \quad (6)$$

At linear geometry the electronic eigenfunctions are related to the electronic angular momentum operator as

$$\hat{L}_z|\phi''\rangle = -\Lambda|\phi'\rangle \quad \hat{L}_z|\phi'\rangle = \Lambda|\phi''\rangle \quad (7)$$

with $\Lambda = 1$ for $\text{NH}_2(^2\Pi_u)$. To avoid complex arithmetic, we construct diabatic electronic functions,^{47,48,50}

$$|\phi_{\pm\Lambda}\rangle = \frac{1}{\sqrt{2}}(|\phi'\rangle \pm i|\phi''\rangle) \quad (8)$$

which then become eigenfunctions of $\hat{L}_z$: $\hat{L}_z|\phi_{\pm\Lambda}\rangle = \pm\Lambda|\phi_{\pm\Lambda}\rangle$. Rather than the artificial choice of $\Lambda = 1$ for both linear and nonlinear geometries,⁵⁰ we used the appropriate matrix elements of the electronic angular momentum as a function of nuclear geometry obtained from our earlier ab initio calculations.²⁵

In the diabatic representation defined above, the nuclear wave function can be written as a vector:

$$|\psi\rangle = \begin{pmatrix} |\psi^+\rangle \\ |\psi^-\rangle \end{pmatrix} \quad (9)$$

and the corresponding Hamiltonian can be expressed in a 2×2 matrix form:

$$\hat{H} = \begin{pmatrix} \hat{H}_{++} & \hat{H}_{+-} \\ \hat{H}_{+-} & \hat{H}_{--} \end{pmatrix} \quad (10)$$

where

$$\hat{H}_{\pm\pm} = -\frac{1}{2\mu_R} \frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_r} \frac{\partial^2}{\partial r^2} + \hat{T}_{\text{rot}} + \left(\frac{B+b}{\sin^2 \gamma} - B \right) (\Lambda^2 \mp 2\Lambda\hat{J}_z) + (V' + V'')/2 \quad (11a)$$

$$\hat{H}_{+-} = (V' - V'')/2 \quad (11b)$$

The adiabatic PESs of the two states (V' and V'') were calculated recently using the high-level ab initio method^{24,25} and were employed in this work for the spectroscopic and dynamical calculations.

Essentially the same discretization scheme was used as in our previous work.^{39,51} Briefly, for R and r , equidistant grids were defined and the actions of the corresponding kinetic energy operators onto the wave function were calculated using the fast sine Fourier transformation method. For the angular degrees of freedom, the following parity (p) adapted FBR (finite basis representation) was used,

$$|j\Omega; Jp\rangle = (2 + 2\delta_{\Omega,0})^{-1/2} (|J\Omega\rangle |j\Omega\rangle + p(-1)^J |J - \Omega\rangle |j - \Omega\rangle) \quad (12)$$

where $|j\Omega\rangle \equiv \Theta_{j\Omega}(\gamma, 0)$ are normalized associated Legendre functions with the Condon–Shortley phase convention,⁵² and $|J\Omega\rangle = [(2J+1)/8\pi^2]^{1/2} D_{\Omega,0}^J$ represents the overall rotation, where $D_{\Omega,M}^J$ is the Wigner rotational matrix.⁵³ The projection of J and j onto the z -axis in the BF frame, Ω , is thus restricted to be non-negative. All Coriolis coupling terms, which couple adjacent helicity channels with different Ω values, were included in the Hamiltonian. The evaluation of the action of the rotational kinetic energy operator is straightforward in this FBR as the operator can be expressed as a tridiagonal matrix. A pseudo-spectral transformation^{54,55} between the FBR and discrete variable representation (DVR) was performed to calculate the action of PES operator, in which the DVR was defined by the angular Gauss–Legendre quadrature points associated with rotational basis $|j\Omega\rangle$.⁵⁶ This approach differs somewhat from that used by Goldfield et al.⁵⁰ in that we can better take advantage of the existing machinery of the angular DVR-FBR transformation and used the ab initio expectation values of the electronic angular momentum operator.

B. Reaction Dynamics with Chebyshev Propagation. The S -matrix element from an initial reactant state (i) to a final product state (f) is expressed as a discrete Fourier transform of the Chebyshev cross-correlation functions:⁵¹

$$S_{f \leftarrow i}^p(E) = \frac{1}{2\pi H^- \sin \vartheta a_i(E) a_f^*(E)} \sum_{k=0} (2 - \delta_{k,0}) e^{-ik\vartheta} C_k^{(f-i)} \quad (13)$$

where the Chebyshev angle is related to the scaled energy by $\vartheta = \arccos E_{\text{scaled}}$,⁵⁷ and $a_i(E)$ and $a_f(E)$ are the energy amplitudes of the initial and final state wave packets, respectively. The correlation functions for the title reaction are defined on the ground ($\tilde{X}^2A''$) adiabatic state as follows:⁵¹

$$C_k^{(f-i)} = \frac{1}{\sqrt{2}} \langle \varphi_{v_f j_f} | \langle JM j_f l_f | (\psi_k^+ - \psi_k^-)_{R=R_\infty} \rangle \quad (14)$$

where R_∞ defines the location in the product ($\text{NH} + \text{H}$) arrangement channel where the projection is made and $|\varphi_{v_f j_f}\rangle$ is the product ro-vibrational wave functions. Note that the angular basis in eq 14 is defined in SF, which allows the use of Hankel functions as the asymptotic basis.⁵¹ The Chebyshev wave packet $|\psi_k\rangle = T_k(\hat{H}_{\text{scaled}})|\psi_0\rangle$ was propagated by a modified three-term Chebyshev recursion relation:^{58,59}

$$|\psi_{k+1}\rangle = D(2\hat{H}_{\text{scaled}}|\psi_k\rangle - D|\psi_{k-1}\rangle) \quad (15)$$

with $|\psi_1\rangle = D\hat{H}_{\text{scaled}}|\psi_0\rangle$. The initial wave packet is assumed to be on the lower ($\tilde{X}^2A''$) adiabat: $|\psi_0\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} |\chi_i\rangle \\ -|\chi_i\rangle \end{pmatrix}$, to compare with the adiabatic reaction dynamics on the $\tilde{X}^2A''$ state. To avoid the divergence outside the range $[-1, 1]$, the Hamiltonian in eq 15 and the energy were properly scaled

$$\hat{H}_{\text{scaled}} = (\hat{H} - H^+)/H^- \quad (16a)$$

$$E_{\text{scaled}} = (E - H^+)/H^- \quad (16b)$$

Here, the spectral medium and half-width of the Hamiltonian $H^\pm = (H_{\text{max}} \pm H_{\text{min}})/2$ were calculated from the spectral extrema, H_{max} and H_{min} , which can be readily estimated. To minimize the spectral range and thus the propagation steps, the potential energy is cut off at a predetermined value. The rotational kinetic energy operator is also limited to this value. To this end, the wave function in the BF FBR was transformed to the space-fixed (SF) frame and then transformed back to BF FBR after applying a truncation to the operator.⁵¹

The following damping function D was applied at the grid edges to impose the outgoing wave boundary conditions:

$$D(x) = \begin{cases} 1 & \text{for } x \leq x_d \\ e^{-d_s(x - x_d)^2} & \text{for } x > x_d \end{cases} \quad (x = R, r) \quad (17)$$

The initial wave packet $|\chi_i\rangle$ in the reactant arrangement channel was taken as a product of a well-defined ro-vibrational eigenfunction $|\varphi_{v_j i}\rangle$ of the diatomic reactant H_2 , a SF angular momentum eigenstate in the coupled representation ($|JM j_i l_i\rangle$), and a one-dimensional Gaussian-shaped wave packet along the $\text{N}-\text{H}_2$ translational coordinate. In particular, the following form in the reactant Jacobi coordinates (R', r', γ') was used

$$|\chi_i\rangle = N e^{-(R' - R'_0)^2/2\delta^2} \cos k_0 R' |\varphi_{v_j i}\rangle |JM j_i l_i\rangle \quad (18)$$

where k_0 , R'_0 , and δ are its mean momentum, position, and width, respectively, and N is the normalization constant. v_i and j_i stand

for the vibrational and rotational quantum numbers of reactant diatomic molecule (H_2), respectively. In practice, this wave function needs to be transformed to the product Jacobi coordinates before propagation. We note that since the initial wave packet is real, the propagation in eq 15 can be carried out entirely with real algebra,⁶⁰ which represents significant savings over the complex time propagation.

The state-to-state differential cross section (DCS) is given by⁶¹

$$\frac{d\sigma_{v_j, v_{j_i}}(\theta, E)}{d\Omega} = \frac{1}{8k_{v_{j_i}}^2} \frac{1}{(2j+1)} \sum_{\Omega, \Omega_i} [|f_+(\theta, E)|^2 + |f_-(\theta, E)|^2] \quad (19)$$

where θ is the scattering angle in the SF frame and

$$f_+(\theta, E) = \sum_{J_p} (2J+1) d_{\Omega, \Omega_i}^J(\pi - \theta) S_{v_j, \Omega_f - v_{j_i}, \Omega_i}^{J_p}(E) \quad (20a)$$

$$f_-(\theta, E) = \sum_{J_p} p(2J+1) d_{\Omega, \Omega_i}^J(\theta) S_{v_j, \Omega_f - v_{j_i}, \Omega_i}^{J_p}(E) \quad (20b)$$

where $d_{\Omega, \Omega_i}^J(\theta)$ is the reduced rotational matrix.⁵³ The j, Ω -specified S -matrix elements are obtained by a transformation between the BF and SF frames:⁶¹

$$S_{v_j, \Omega_f - v_{j_i}, \Omega_i}^{J_p} = \sum_{l, l_f} (U_{l, \Omega_f}^{J_p})^* S_{v_j, l_f - v_{j_i}, l_i}^{J_p} U_{l, \Omega_i}^{J_p} \quad (21)$$

with

$$U_{l, \Omega}^{J_p} = \frac{i^l}{\sqrt{2(1 + \delta_{\Omega, 0})}} [\langle j, \Omega, J - \Omega | l, 0 \rangle + p(-1)^J \langle j - \Omega, J | l, 0 \rangle] \quad (22)$$

Here, $\langle \dots, l, \dots \rangle$ denotes the Clebsch–Gordan coefficient.⁵³

Finally, the state-to-state integral cross section (ICS) can be expressed as follows:

$$\sigma_{v_j, v_{j_i}}(E) = \frac{\pi}{(2j_i + 1)k_{v_{j_i}}^2} \sum_{J, p, l_i, l_f} (2J+1) |S_{v_j, \Omega_f - v_{j_i}, \Omega_i}^{J_p}(E)|^2 \quad (23)$$

C. Bound State Calculations. The ro-vibrational states of the RT coupled $\tilde{A}/\tilde{X}$ system of NH_2 were determined using the same Hamiltonian discussed in section IIB. However, the Lanczos algorithm⁶² was used to obtain energy levels up to $J = 3$. Briefly, a random initial wave packet was used to start the three term Lanczos iteration, which yields a tridiagonal matrix. The diagonalization of the tridiagonal matrix gives approximate eigenvalues. Details of this method including a procedure to eliminate spurious eigenvalues can be found in ref 57.

III. Results and Discussion

The numerical parameter has been determined after convergence test calculations for $J = 0$. The chosen values are listed

in Table 1. Note that the numerical parameters used here are different between reaction dynamical calculations and bound state energy level calculations. In the dynamical calculations, the same numerical parameters were used for both the single state calculations and RT coupled two state calculations. In addition, all partial waves up to $J = 37$ were included in the reaction dynamical calculations.

A. Bound States. In our earlier publications,^{24,25} vibrational states on both the ground ($\tilde{X}^2A'$) and excited ($\tilde{A}^2A'$) state PESs of NH_2 have been determined. The agreement with known experimental band origins was generally satisfactory, and much better than the other global PESs used for reaction dynamics. In particular, it was shown that the diagonal RT term is very important in reproducing the low-lying experimental vibrational levels on the quasi-linear $\tilde{A}^2A'$ state.²⁵ Here, we extend the previous work to $J > 0$, with inclusion of the nonadiabatic RT coupling.

The ro-vibronic energy levels have been calculated for $J = 1-3$ with and without the RT coupling. Due to space limitation the list of energy levels is not presented here. Assignment of every line proved to be a difficult task because of the mixing between electronic states and among various vibrational modes. The structure of the asymmetric top rotational spectrum further complicated the issue. To assess the accuracy of the PESs, particularly the excited $\tilde{A}^2A'$ state, we focus here on the lowest vibrational state (0, 0, 0). This state is close to linearity and thus the RT coupling is expected to play an important role. In Table 2 the calculated energies are compared to the experimental energy levels.⁶³ Note that all the energy levels have chosen the values relative to energy of their own $J = 0$ vibrational states. As shown by the comparison, the inclusion of the RT coupling significantly improves the agreement with experimental measurements. Furthermore, the improvement becomes more significant with the increase of the J value, underscoring the importance of the RT coupling to the NH_2 rovibrational energy levels.

B. Reaction Probabilities and Integral Cross Sections. The total reaction probabilities for several J values are displayed in Figure 1, obtained with and without the RT coupling. The former was calculated using the ground $\tilde{X}^2A'$ state Born–Oppenheimer PES. The results show similar qualitative features. For example, both $J = 0$ probabilities have small thresholds due apparently to the potential energy barrier in the entrance channel. Due to the relatively small reduced mass, the tunneling effect is expected to be important, especially at low temperatures, underscoring the importance of the quantum approach. Despite the dominance of the deep well, the energy dependence shows small oscillatory structures superimposed on a broad background. These weak oscillations are presumably resonances that are short-lived due to the large exothermicity. The threshold energy increases with J due to the centrifugal energy barrier. The comparison between the reaction probabilities with and without the RT coupling clearly shows differences. However, the reactivity is on averaged little affected, implying that the RT effect is probably insignificant in total reactivity.

In Figure 2, the total and product vibrational state resolved integral cross sections (ICSs) calculated with and without RT coupling are displayed. Again the qualitative features are similar whether the RT coupling is included or not. The vibrational state resolved ICSs show clear thresholds and they increase monotonically with the collision energy. The vibrational state resolved ICSs for low v_f states level off at higher energies while the total ICS increases even at the highest energies due to the opening of higher vibrational channels. At a given collision

TABLE 1: Numerical Parameters Used in the Calculations (Atomic Units Used unless Specified Explicitly)

	reaction dynamics calculations	bound state calculations
grid/basis range and size	$R \in (0.5, 15)$ ($N_R = 127$) $r \in (0.5, 15)$ ($N_r = 127$) $j = 0$ to $j_{\max} = 99$ ($N_j = 100$ over $\gamma \in (0, 180^\circ)$)	$R \in (0.5, 8)$ ($N_R = 99$) $r \in (0.5, 8)$ ($N_r = 99$) $j = 0$ to $j_{\max} = 79$ ($N_j = 80$ over $\gamma \in (0, 180^\circ)$)
damping	$e^{-0.005(R-11)^2}$ for $R > 11$ $e^{-0.005(r-11.5)^2}$ for $r > 11.5$ $= 1$ otherwise	N/A
initial wave packet ($e^{-((R-R_0)/\delta)^2/2} \cos(k_0 R)$)	$R_0 = 9.0$ eV $E_0 = \hbar^2 k_0^2 / 2\mu = 0.12$ eV $\delta = 0.15$	Random wavepacket
spectral control	energy cut of 0.4 hartree (PES and each rotational kinetic energy terms)	same as left
final state projection	$R_\infty = 8.0$	N/A
propagation steps	25k	40k

TABLE 2: Comparison of Experimental and Calculated Energy Levels of the Rotational Energy States Associated with the $\tilde{A}^2A'$ (0, 0, 0) State

(J, K_a, K_c)	expt ⁶³	theo w/ RT	theo w/o RT	diff w/ RT	diff w/o RT
(0, 0, 0)	0	0	0	0	0
(1, 0, 1)	17.5495	19.47	17.42651	1.9205	0.122992
(1, 1, 0)	203.082	213.5422	216.5476	10.4602	13.46559
(1, 1, 1)	203.6095	213.5424	217.4094	9.9329	13.79989
(2, 0, 2)	52.683	55.65919	52.26971	2.976192	0.413293
(2, 1, 1)	240.519	234.4496	250.8256	6.069432	10.30658
(2, 1, 2)	242.1105	236.0053	253.4118	6.105205	11.30128
(2, 2, 0)	568.7	568.3417	587.9125	0.358323	19.21249
(2, 2, 1)	568.7495	568.5074	587.9145	0.242098	19.16501
(3, 0, 3)	105.212	113.9525	104.5101	8.740472	0.701919
(3, 1, 2)	294.696	296.373	302.2275	1.676976	7.531514
(3, 1, 3)	297.964	296.7355	307.3905	1.228519	9.426486
(3, 2, 1)	624.088	623.2603	640.9863	0.827654	16.89832
(3, 2, 2)	624.303	624.0819	640.9965	0.221092	16.69353
(3, 3, 0)	1029.912	1027.572	1060.836	2.33991	30.92434
(3, 3, 1)	1029.863	1028.199	1060.836	1.663554	30.97323

energy, the vibrational distribution of the NH product decays monotonically with the vibrational quantum number, consistent with the insertion mechanism. Quantitatively, the RT effect is non-negligible. At some energies, the RT coupling enhances the reactivity and at some other energies it reduces the reactivity. On average, the reactivity is little affected. The RT effect to the product vibrational state resolved ICSs is more significant than that to the total ICS.

The relatively small effect of the RT coupling on reactivity observed here is consistent with previous results obtained by other theoretical groups.^{40–43} This small RT effect can largely be attributed to the fact that the reaction takes place at much higher energies than where the two PESs become degenerate. Hence, the majority of the reaction flux tends to stay adiabatic because of the short “time” spent near the crossing seam.⁴⁰ Nevertheless, it should be emphasized that our investigations in this work were limited to the reaction process starting from the $\tilde{X}^2A''$ adiabat in the $N + H_2$ reactant channel. There is also a contribution from the $\tilde{A}^2A'$ adiabat, which is not considered here because of its smallness.^{18,40} In the latter case, the reaction to the $NH(X^3\Sigma^-) + H$ product can only proceed via RT coupling. As noted by Petrongolo and co-workers,^{41,43} this nonadiabatic channel becomes substantially more important for ortho- H_2 , due to nuclear spin statistics.

C. Product Rotational State Distributions. In Figure 3, product rotational state distributions for several selected collision energies are displayed with and without the RT coupling. Both results show highly inverted rotational distributions with peaks occurring near the maximum allowed rotational quantum

numbers. These features are again consistent with the complex-forming mechanism. Due to energy constraints, the peak of the rotational distribution shifts to lower rotational quantum numbers with increasing vibrational quantum number. As the collision energy increases, the distributions shift to higher rotational quantum numbers.

The RT effect is again not significant, except at the lowest collision energy. At 0.05 eV, the population for low rotational states is affected by RT quite significantly. This is probably due to the fact that the energy is closer to the RT region, which allows the reaction complex to have a higher probability for nonadiabatic transitions. In addition, the final rovibrational resolved ICS is less averaged compared to total ICS and vibrational state resolved ICSs. However, we note that the cross section at this threshold energy is quite low.

D. Differential Cross Sections. The differential cross section (DCS), or the product angular distribution, provides the most detailed information about a reaction. This experimentally observable attribute has not been calculated before for a RT coupled system using a quantum mechanical method. The comparison between the DCSs with and without RT coupling is given in Figure 4 for several collision energies. Both angular distributions are peaked at two extremal angles (0° and 180°) at all energies, consistent with the complex-forming mechanism of the reaction.

Interestingly, the RT effect manifests quite significantly in the product angular distribution near the two extreme directions. The inclusion of the RT effect consistently reduces the distribution for both the backward and forward scattering. Moreover,

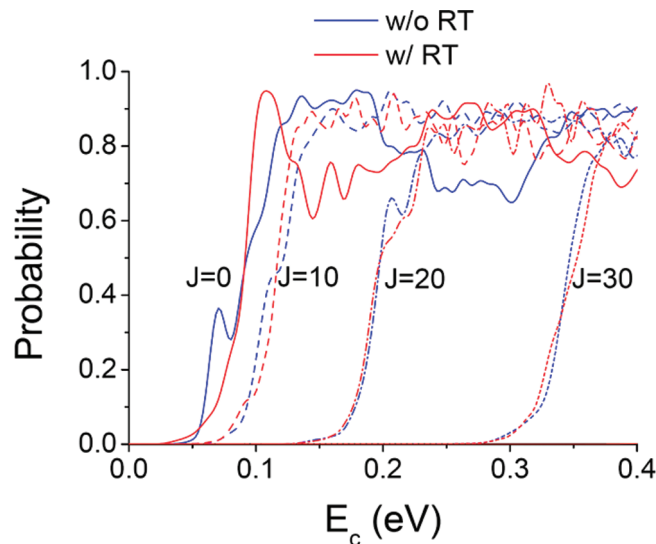


Figure 1. Total reaction probabilities for several chosen J values with (red) and without (blue) the RT coupling.

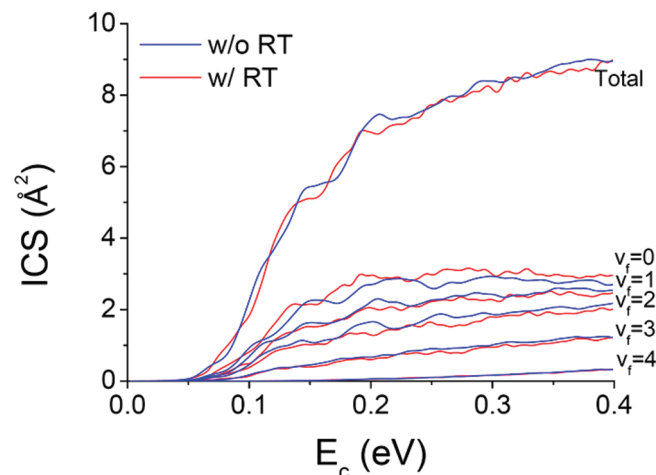


Figure 2. Total and product vibrational state resolved ICSs with (red) and without (blue) the RT coupling.

the backward is more affected. As a result, the backward direction ($\theta \sim 180^\circ$) bias observed on the adiabatic $\tilde{X}$ -state PES almost disappeared, leading to a more symmetric angular distribution. With the increase of collision energy, this effect becomes less remarkable. Despite the relatively large RT effect on the DCSs, the ICS have shown small RT effect, which is due to the small weight ($\sin \theta$) in the backward and forward directions.

IV. Conclusions

The influence of nonadiabatic coupling in reaction dynamics has attracted much recent attention.⁶⁴ However, most of the recent nonadiabatic quantum scattering studies have concentrated on conical intersections^{65–68} and intersystem crossing.^{69,70} Renner–Teller (RT) coupling is quite common in reactive systems, and their effects on dynamics are less well understood. In this work, we report the first state-to-state quantum study of the $\text{N}(^2\text{D}) + \text{H}_2(\tilde{X}^1\Sigma_g^+) \rightarrow \text{NH}(\tilde{X}^3\Sigma^-) + \text{H}(^2\text{S})$ reactive system affected by the RT interaction, using recently developed ab initio global PESs. The results in this prototypical system will help us to understand other reactive RT systems such as HO_2 , CH_2 , and HCO .

To understand the influence of the RT coupling on the reaction dynamics, we compare reaction probabilities, product

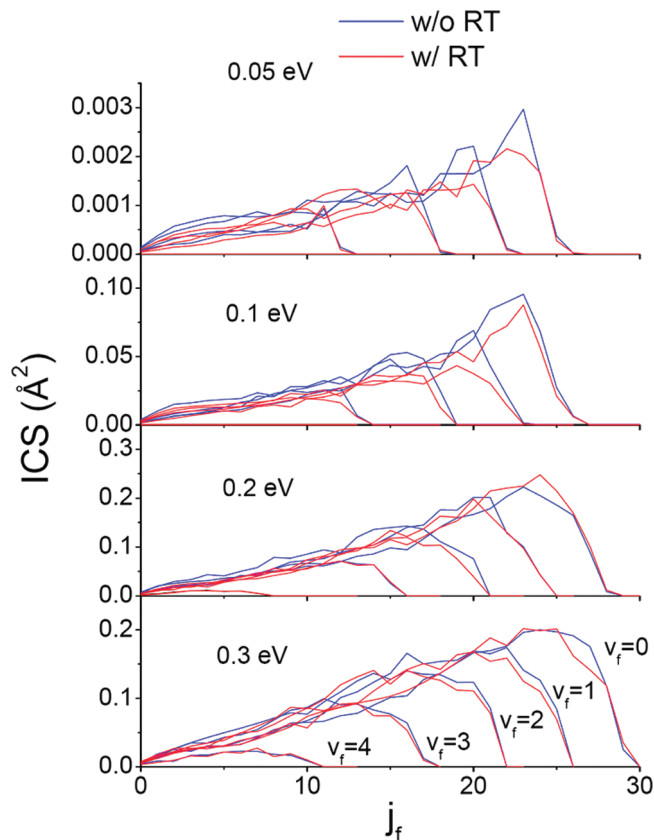


Figure 3. Product rovibrational state resolved ICSs at four selected collision energies with (red) and without (blue) the RT coupling.

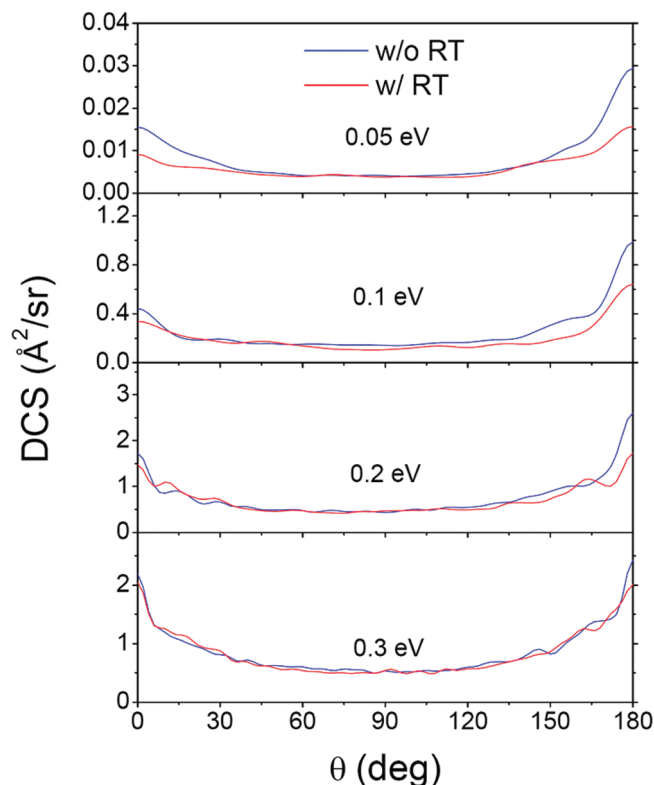


Figure 4. Total DCSs at four selected collision energies with (red) and without (blue) the RT coupling.

internal state distributions, and product angular distributions obtained with and without the RT coupling. To facilitate a meaningful comparison, only the scattering process starting from

the ground ($\tilde{X}^2A''$) state adiabatic PES was investigated. It was found that the RT coupling has a limited impact on most measurable quantities such as total integral cross section and product internal state distributions. This observation is consistent with previous theoretical work on this system. However, discernible differences can be found at low collision energies, at which the system presumably has more time to make nonadiabatic transitions.

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