Experimental and theoretical investigations of the reactions

\( \text{NH}(X^3\Sigma^-) + \text{D}(^2S) \rightarrow \text{ND}(X^3\Sigma^-) + \text{H}(^2S) \) and

\( \text{NH}(X^3\Sigma^-) + \text{D}(^2S) \rightarrow N(^4S) + \text{HD}(X^1\Sigma^+_g) \)

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The rate coefficient of the reaction \( \text{NH}(X^3\Sigma^-) + \text{D}(^2S) \rightarrow \text{ND}(X^3\Sigma^-) + \text{H}(^2S) \) is determined in a quasistatic laser-flash photolysis, laser-induced fluorescence system at low pressures. The \( \text{NH}(X) \) radicals are produced by quenching of \( \text{NH}(a^1\Delta) \) (obtained in the photolysis of \( \text{HN}_3 \)) with Xe and the D atoms are generated in a D\textsubscript{2}/He microwave discharge. The \( \text{NH}(X) \) concentration profile is measured in the presence of a large excess of D atoms. The room-temperature rate coefficient is determined to be \( k_1 = (3.9 \pm 1.5) \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \). The rate coefficient \( k_1 \) is the sum of the two rate coefficients, \( k_{1a} \) and \( k_{1b} \), which correspond to the reactions \( \text{NH}(X^3\Sigma^-) + \text{D}(^2S) \rightarrow \text{ND}(X^3\Sigma^-) + \text{H}(^2S) \) (1a) and \( \text{NH}(X^3\Sigma^-) + \text{D}(^2S) \rightarrow \text{N}(^4S) + \text{HD}(X^1\Sigma^+_g) \) (1b), respectively. The first reaction proceeds via the \( ^2A'' \) ground state of \( \text{NH}_2 \) whereas the second one proceeds in the \( ^4A'' \) state. A global potential energy surface is constructed for the \( ^4A'' \) state using the internally contracted multireference configuration interaction method and the augmented correlation consistent polarized valence quadrupole zeta atomic basis. This potential energy surface is used in classical trajectory calculations to determine \( k_{1a} \). Similar trajectory calculations are performed for reaction (1b) employing a previously calculated potential for the \( ^4A'' \) state. The calculated room-temperature rate coefficient is \( k_1 = 4.1 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) with \( k_{1a} = 4.0 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) and \( k_{1b} = 9.1 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \). The theoretically determined \( k_1 \) shows a very weak positive temperature dependence in the range 250 \( \leq T/K \leq 1000 \). Despite the deep potential well, the exchange reaction on the \( ^2A'' \) ground-state potential energy surface is not statistical. © 2005 American Institute of Physics.

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I. INTRODUCTION

\( \text{NH}_i \) \( (i = 1, 2) \) radicals are of great importance for understanding the nitrogen chemistry in flames.\textsuperscript{1,2} The amino radical \( \text{NH}_2 \) is essential in nitrogen flame chemistry such as its isoelectronic counterparts \( \text{OH} \) and \( \text{CH}_2 \) in combustion chemistry. In the present investigation, experimental information on the association-dissociation reaction of \( \text{NH}_2(\tilde{X}) \) is obtained via a detour, namely, the reaction of ground-state NH radicals with D atoms.

\begin{equation}
\text{NH}(X^3\Sigma^-) + \text{D}(^2S) \rightarrow \text{products}, \quad (1)
\end{equation}

The complementary reaction with hydrogen atoms, i.e.,

\begin{equation}
\text{NH}(X^3\Sigma^-) + \text{H}(^2S) \rightarrow \text{products}, \quad (2)
\end{equation}

which has been studied experimentally and theoretically in Ref. 3 (hereafter termed paper I), provides information only on the production of \( \text{N}(^4S) \) atoms. Reaction (2) proceeds on the potential energy surface (PES) of the quartet state \( ^4A'' \) (\( ^4\Sigma^- \) in linear \( \text{N}–\text{H}–\text{H} \) configuration; Fig. 1) with a measured rate coefficient \( k_2(298 \text{ K}) = 1.9 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \). The reaction on the doublet PES, \( ^2A'' \), leading to \( \text{NH}_2(\tilde{X}) \) cannot be observed in reaction (2), because the initially formed complex decomposes to the educts \( \text{NH}(X^3\Sigma^-) \) and \( \text{H}(^2S) \).

The pathway via the \( \text{NH}_2(\tilde{X}) \), respectively, \( \text{ND}(\tilde{X}) \) ground state can be investigated, however, via reaction (1). It encompasses two different reaction paths that both lead to a depletion of \( \text{NH}(X^3\Sigma^-) \) :

\begin{equation}
\text{NH}(X^3\Sigma^-) + \text{D}(^2S) \rightarrow \text{ND}(X^3\Sigma^-) + \text{H}(^2S), \quad (1a)
\end{equation}

\begin{equation}
\text{NH}(X^3\Sigma^-) + \text{D}(^2S) \rightarrow \text{N}(^4S) + \text{HD}(X^1\Sigma^+_g). \quad (1b)
\end{equation}

The \( 
\text{N}(^2D) + \text{HD}(X^1\Sigma^+_g) \) channel is not accessible at the temperatures considered in this work. The first reaction proceeds on the \( ^2A'' \) PES while the second one occurs on the \( ^4A'' \) PES. If Renner–Teller (RT) coupling between the \( ^2A'' \) and \( ^4A'' \) states is ignored, each reaction can be considered as a one-state problem. Reaction (1a) is expected to be much faster than reaction (1b), because the \( ^2A'' \) PES is rather attractive and the reaction is not constrained to near-linear approaches...
as it is on the $^4A^\prime$ PES. Consequently, $k_1$ is expected to be considerably larger than $k_2$. Reaction (1) has not yet been studied directly, neither experimentally nor theoretically.

In the present work we measure the rate coefficient for reaction (1) at room temperature via the depletion of NH(X) radicals (Sec. II). We construct a global PES for the $^4A^\prime$ state by electronic structure calculations (Sec. III) and perform classical trajectory calculations on this PES in order to determine $k_{1a}$ (Sec. IV). The rate coefficient $k_{1a}$ is evaluated by trajectory calculations using the $^4A^\prime$ PES constructed in paper I. The conclusions which can be drawn from the joint experimental and theoretical studies are given in Sec. V.

II. EXPERIMENTAL RESULTS

The experiment is performed, as described in paper I, in a quasistatic laser-flash photolysis/laser-induced fluorescence (LIF) system, where “quasistatic” means that the flow through the reaction cell is negligible between the pump and the probe pulses, but sufficient to exchange the gas volume between two subsequent pump pulses. The carrier gas is He at a total pressure of 6.9 mbar $\leq p \leq 14.2$ mbar.

The experimental setup is described in paper I and in detail elsewhere, thus only the keywords are given here. For the photolysis a XeCl-exciplex laser with pulse energies in the range of 200–400 mJ and a beam area of about 1.1 cm$^2$ is used. The probe laser is a dye laser with a beam area of 7 mm$^2$. It is pumped by an exciplex laser.

The NH(X) radicals are obtained by quenching NH($a^1\Delta$) with Xe and the NH(a) radicals are produced by HN$_3$ photolysis. The D atoms are generated in a sidearm of the reactor in a microwave discharge of a D$_2$/He mixture (0.02–0.03 molfraction D$_2$ in He). The absolute initial D atom concentration is determined via titration with NO$_2$. The increase of OD with increasing NO$_2$ is observed by LIF via the $Q_1(2)$ line of the transition $A^2\Sigma^+ \rightarrow X^2\Pi$, $\nu=0 \rightarrow X^2\Pi$, $\nu=0$ at $\lambda=307.54$ nm with a dye laser pumped by a Nd:YAG (yttrium aluminum garnet) laser. NH(X, $\nu=0$) is detected by exciting the $P_2(2)$ line at $\lambda=336.48$ nm of the transition $A^2\Pi \rightarrow X^2\Pi$.

Typical NH(X) concentration profiles in the absence (○) and presence (●) of D atoms.

\[ A^3\Pi, \nu'=0 \rightarrow X^3\Sigma^+, \nu'=0. \]  

The undispersed fluorescence from the excited state is observed in the wavelength range of 335–337 nm perpendicular to the laser beam.

The HN$_3$ and Xe are added to the reactor via an inner probe which ends about 1 cm above the photolysis volume. The NO$_2$ for the titration is also added to the system through this probe. Gases with the highest commercially available purity are used: He, 99.9999%, Praxair; Xe, 99.998%, Messer-Griesheim; N$_2$, 99.995%, UCAR; D$_2$, 99.7% (rest H$_2$), Messer-Griesheim; and NO$_2$, 99.5%, Merck. HN$_3$ is synthesized by melting stearic acid, CH$_3$(CH$_2$)$_{16}$COOH (97%, Merck), with NaN$_3$ (99.0%, Merck).

The NH(X) radicals are produced in the fast quenching reaction

\[ \text{NH}(a^1\Delta) + \text{Xe} \rightarrow \text{NH}(X^3\Sigma^-) + \text{Xe}. \]  

Typical NH(X) concentration profiles in the absence and in the presence of D atoms are shown in Fig. 2. NH(a) is formed at $t=0$ by the photolysis pulse. In both cases (with or without D atoms present), the NH(X) concentration increases very rapidly in time due to the quenching of NH(a) by Xe. In the absence of D atoms (discharge off, open circles in Fig. 2) the NH(X) concentration stays constant after about 12$\equiv t/\mu s\equiv 23$ (depending on the Xe concentration) for more than 300 $\mu$s. This means that neither diffusion nor the other gases present in the system (D$_2$ and HN$_3$) contribute to the NH(X) consumption (as expected from the rates and concentrations of these molecules). For the individual experiments the Xe concentration is in the range 0.9$\leq [\text{Xe}] / 10^{-8} \text{ mol cm}^{-3} \leq 1.9$, as given in Table I. The dashed line in Fig. 2 is obtained from a simple simulation of the system assuming an initial NH(a) concentration of $[\text{NH}(a)]_0=2.6 \times 10^{-13} \text{ mol cm}^{-3}$ estimated from the HN$_3$ absorption at the photolysis wavelength and a dissociation quantum yield of one. The subsequent analysis of the NH(X) profiles to determine $k_1$ start at about $t>12 \mu s$ depending on the particular experimental conditions.

The NH(X) concentration profile in Fig. 2 in the presence of D atoms (full dots) shows a depletion which is due to reaction (1). The line is the result of a simulation including reaction (1). The D atom concentration is large compared to

![FIG. 1. Schematic energy level and correlation diagram for the reaction NH($X^3\Sigma^\ast$) + HI($S^\ast$) → products. The energies and transition state geometries are the ones calculated in this work (aug-cc-pvqz atomic basis). The conical intersection of the $^4A^\prime$ state with a higher state of the same symmetry is indicated; for a more complete representation, see Ref. 29.](image1)

![FIG. 2. Typical NH(X) concentration profiles in the absence (○) and presence (●) of D atoms.](image2)
The reactions \( \text{NH}(X^3\Sigma^-) + \text{D}(^2S) \rightarrow \text{ND}(X^3\Sigma^-) + \text{H}(^2S) \) are studied.

The slope of \( \ln \text{f} \) and thus pseudo-first-order conditions are realized. From the slope of \( \ln \text{f} \) versus time first-order rate coefficients \( k_{\text{eff}} \) are determined by

\[
\frac{d\ln[\text{NH}(X)]}{dt} = k_{\text{eff}} [\text{D}],
\]

This \( k_{\text{eff}} \) is converted with the measured D atom concentrations into the second-order rate coefficients \( k_{1} \).

The results for the 21 independent experiments are summarized in Table I. It is not possible to vary the D atom concentration over a wide range (a factor of 2.4 was realized) and therefore the dependence of the first-order rate coefficient versus [D] cannot be investigated. For the fifth experiment in Table I a rate coefficient is obtained which is much larger than those deduced from the other experiments. We attribute less than 5% to the overall NH(X) consumption.

### Table I. Experimental data for the 21 independent experiments.

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<th>( p ) (mbar)</th>
<th>([\text{Xe}] \times 10^8) mol/cm(^3)</th>
<th>([\text{D}_2] \times 10^8) mol/cm(^3)</th>
<th>([\text{H}_2\text{N}] \times 10^{11}) mol/cm(^3)</th>
<th>([\text{D}] \times 10^{10}) mol/cm(^3)</th>
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<th>( k_{1} \times 10^{-13}) cm(^3)/mol s</th>
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The electronic structure calculations for the two lowest states of NH\(_2\): the ground state \( \tilde{X}^2A^\prime \) and the first excited state \( \tilde{A}^2A^\prime \) (see Fig. 1). Only the ground state is relevant for the present study. However, the \( \tilde{X}^2A'' \) and \( \tilde{A}^2A' \) states form a RT pair i.e., they are degenerate for linear geometries, and therefore it is reasonable to consider them together. The first excited electronic state is required for studying the depletion of NH in the first excited state, \( a^1\Delta \), in collisions with hydrogen atoms. Global PESs for the \( \tilde{X}^2A'' \) and \( \tilde{A}^2A' \) states of NH\(_2\) have been previously calculated by Pederson \( et al. \), and Ho \( et al. \). These PESs have been used in several classical and quantum-mechanical calculations. The Jacobi coordinates appropriate for the N+H\(_2\) channel: \( R \), the distance from N to the center of mass of H\(_2\); \( r \), the H\(_2\) bond distance; and \( \gamma \), the angle between the vectors \( \mathbf{R} \) and \( \mathbf{r} \). If not stated otherwise, energy is normalized such that \( E=0 \) corresponds to \( \text{NH}(X^3\Sigma^-) + \text{H}(^2S) \) with NH at equilibrium.

### A. Electronic structure calculations

The electronic structure calculations for the \( \tilde{X}^2A'' \) and \( \tilde{A}^2A' \) states are performed on the same level of theory, as described in paper I for the \( ^4A'' \) state. The internally con-
programs. The present electronic structure calculations are
zeta augmented correlation consistent polarized valence triple
that the atomic basis is larger, i.e., aug-cc-pvqz compared to
first calculate, using several basis sets, the critical points on
95/115 reference configuration state functions for the
lations. There are 45/81 reference configurations with
CASSCF calculations but frozen in the subsequent CI calcu-
field
mized full-valence complete-active space self-consistent-
orbital of nitrogen is fully optimized in the
20,21 If not stated otherwise, the
aug-cc-pvtz
s
aug-cc-pvqz
d
aug-cc-pv5z
aug-cc-pv6z
Expt.
In order to assess the accuracy of the present study we
A
9
and 2\textsuperscript{A}\textsuperscript{′}
states.
In order to assess the accuracy of the present study we
first calculate, using several basis sets, the critical points on
symmetry using the MOLPRO suit of
symmetry
states.
The data for the three asymptotic channels are given in
Table III and compared with recent theoretical and experi-
mental data. Again, the results converge fast with the basis
size and the agreement with the results of Pederson et al.\textsuperscript{9,10}

<table>
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<th>E\textsuperscript{a}</th>
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\textsuperscript{a}Energies with respect to NH(X\textsuperscript{\textsuperscript{2}Σ\textsuperscript{+}})+H(\textsuperscript{2}S) with NH at equilibrium.
\textsuperscript{b}From Table I of Pederson et al., Ref. 10.
\textsuperscript{c}From Table II of Pederson et al., Ref. 10.
\textsuperscript{d}See text for details.
\textsuperscript{e}From Table I of Pederson et al., Ref. 10; results without Davidson correction.
\textsuperscript{f}Reference 10; results without Davidson correction.
\textsuperscript{g}Reference 24.
\textsuperscript{h}Reference 25.

extracted multireference configuration interaction (MRCI)
method\textsuperscript{17,18} is used. In order to approximately account for
higher excitations and size consistency the Davidson correction is applied.\textsuperscript{19} The MRCI calculations are based on opti-
mized full-valence complete-active space self-consistent-
field (CASSCF) orbitals.\textsuperscript{20,21} If not stated otherwise, the
augmented correlation consistent polarized valence sext-
duple zeta (aug-cc-pvqz) atomic basis set of Dunning\textsuperscript{22} is
employed. The 1s orbital of nitrogen is fully optimized in the
CASSCF calculations but frozen in the subsequent CI calcu-
lations. There are 45/81 reference configurations with
95/115 reference configuration state functions for the
2\textsuperscript{A}\textsuperscript{′}/2\textsuperscript{A}\textsuperscript{′} state leading to 275 346/283 405 contracted con-
figurations in the CI calculations. All calculations are per-
formed in C\textsubscript{x} symmetry using the MOLPRO suit of
programs.\textsuperscript{23} The present electronic structure calculations are
very similar to those of Pederson et al.\textsuperscript{5,10} with the exception that the atomic basis is larger, i.e., aug-cc-pvqz compared to
augmented correlation consistent polarized valence triple
zeta (aug-cc-pv5z).

In order to assess the accuracy of the present study we
first calculate, using several basis sets, the critical points on
the two PESs by full optimization. The equilibrium geomet-
ries and energies of the global minimum of the 2\textsuperscript{A}\textsuperscript{′} and 2\textsuperscript{A}\textsuperscript{′}
states are given in Table II. The convergence with respect to
the atomic basis size is very fast; the results obtained for the
aug-cc-pvqz basis set do not differ much from the results for
the augmented correlation consistent polarized valence sext-
duple zeta (aug-cc-pv6z) basis. The present results agree well
with the results of Pederson et al.\textsuperscript{9,10} obtained with the
aug-cc-pv5z basis. The calculated equilibrium coordinates
also agree well with the experimental data.\textsuperscript{24,25} The energy of
the ground-state minimum with respect to NH(X)+H is cal-
culated using thermodynamical data\textsuperscript{26,27} and the calculated
zero-point energies for NH\textsubscript{2}(\tilde{X}) (0.519 eV) and NH(X)
(0.212 eV). The experimental value of −98.77 kcal/mol
agrees well with the calculated value of −98.48 kcal/mol
with the large aug-cc-pv6z basis set. The experimental ener-
gy of the minimum of the excited state with respect to
NH(X)+H is calculated by using the barriers to linearity of
the \tilde{X} 2\textsuperscript{A}\textsuperscript{′} (11 914 cm\textsuperscript{−1}) and the \tilde{A} 2\textsuperscript{A}\textsuperscript{′}
(863 cm\textsuperscript{−1}) states as determined by Gabriel et al.\textsuperscript{7} (Table 3); the two PESs in Ref.
7 have been constructed in a least-squares procedure to ex-
actly reproduce the measured rovibronic transition energies
and therefore can be considered as accurate. The calculated
value of −67.28 kcal/mol agrees well with the experimental
value of −67.18 kcal/mol.

The data for the three asymptotic channels are given in
Table III and compared with recent theoretical and experi-
mental data. Again, the results converge fast with the basis
size and the agreement with the results of Pederson et al.\textsuperscript{9,10}

<table>
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</table>

\textsuperscript{a}Energies with respect to NH(X)+H.
\textsuperscript{b}From Table II of Pederson et al., Ref. 9.
\textsuperscript{c}From Table I of Pederson et al., Ref. 10; without Davidson correction.
\textsuperscript{d}See text for details.
\textsuperscript{e}Reference 27.
and the $\Delta$ states are doubly degenerate. The $\Pi$ state correlates for small HN–H bond distances with the ground-state minimum and for large HN–H bond distances it correlates with a highly excited state of NH. This leads, for both the $2A''$ and the $2A'$ states, to a complicated pattern of avoided crossings for near-linear geometries, as illustrated in Fig. 3(a) for $\alpha=160^\circ$. For the present study, the depletion of NH($^3\Sigma^-$), only the lowest $2A''$ adiabatic state is of relevance.

The electronic structure in the N+H$_2$ channel is simpler. In Fig. 4 we show cuts through the six lowest PESs (three $2A'$ and three $2A''$ states) as functions of the Jacobi coordinate $R$. The H$_2$ bond distance is fixed at $r=1.42a_0$ and the angle is $\gamma=90^\circ$. No avoided crossing complicates the PESs in this asymptotic channel. The lowest two PESs have small barriers, the geometries and energies of which are listed and compared with previous theoretical predictions in Table IV. The barrier of the ground-state PES is slightly lower than the barrier of the excited-state PES. The present results agree well with the previous data of Pederson et al.\textsuperscript{9,10}

A complication due to a conical intersection occurs, however, at shorter N–H$_2$ bond distances, where the first and the second $2A'$ states cross each other near the $C_{2v}$ configuration.\textsuperscript{29} This is illustrated in Fig. 5 showing potential cuts for the lowest three states with $^2A''$ symmetry, $^1\Sigma^+ A'$, $^2A'$, and $^3A'$. This figure is the continuation of Fig. 4 to

---

**TABLE IV.** Geometries, $R$ and $r$ (in $a_0$), and energies $E$ (in kcal/mol) for the transition state barriers in the N+H$_2$ channel and several basis sets; $\gamma=90^\circ$.

<table>
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<th>$\tilde{A}^2A'$</th>
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<td>3.937</td>
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*Energies with respect to the N($^3\Sigma^-$)+H$_2$ asymptote.

*From Table II of Pederson et al., Ref. 9.

*From Table I of Pederson et al., Ref. 10.
smaller bond distances. A (diabatic) state which correlates with a highly excited product channel of N + H₂ cuts through all the lower (diabatic) states and thus leads to a series of crossings which become avoided crossings in C₅ symmetry. Relevant for our studies of the depletion of NH(X) and NH(a) in collisions with H atoms is only the crossing with the lowest state (R = 1.6a₀), which connects with NH(a) + H(2S). The location of the crossing depends significantly on r as well as γ. In the construction of the ²A' PES (Sec. III B) we do not explicitly take this avoided crossing into account but merely consider the lowest adiabatic state with ²A' symmetry.

**B. Construction of potential energy surfaces**

The global three-dimensional PESs for the lowest ²A' and the lowest ⁴A'' states are calculated employing the aug-cc-pvqz basis set, which is a reasonable compromise between accuracy and computational cost. Because our primary focus is the reaction of H atoms with NH(X) radicals, we choose the two H–N bond distances R₁ and R₂ and the H–N–H angle α as coordinates for the main three-dimensional grid. Note, these coordinates are different from those used in paper I to calculate the ⁴A'' PES, which has a transition state (TS) at linear N–H–H geometries. The N–H bond lengths (in a₀) are varied between 1.3 and 2.6, 2.8 and 5.0, 5.0 and 6.0, and 7.0 and 9.0 with step sizes of 0.1, 0.2, 0.5, and 1.0, respectively, and α (in degrees) is varied from 0 to 180 with a step size of 10. Additional calculations are performed for 176° for a better description of near-linear geometries. This grid consists of a total of 9424 independent grid points.
The grid defined in the coordinates $R_1$, $R_2$, and $\alpha$, however, is not appropriate for representing the global PES in and near the $N(3S)+H_2$ channel, that is, in the region of small values of $\alpha$. Therefore, we define a second grid in terms of the Jacobi coordinates $R$, $r$, and $\gamma$ suitable for the $N+H_2$ channel. $R$ ($in\alpha_0$) is varied from 1.8 to 2.6, 2.8 to 5.0, 5.0 to 5.5, and 6.0 to 9.0 with step sizes of 0.1, 0.2, 0.5, and 1.0, respectively. The $H_2$ bond length ($in\alpha_0$) is varied between 0.9 and 2.2 and 2.4 and 3.0 with step lengths of 0.1 and 0.2, and the Jacobi angle $\gamma$ is varied from 10 to 90° with a step size of 10°; additional calculations are performed at 2°. The second grid comprises a total of 4680 points.

Analytical representations for both PESs and both grids are obtained separately by three-dimensional cubic spline interpolation. If $V_1$ and $V_2$ denote the two potential representations on the bond-coordinate and the Jacobi-coordinate grids, respectively, combined potentials are constructed by

$$V = \begin{cases} V_1 & \text{for } r \geq 3\alpha_0 \\ V_1 f + V_2 (1 - f) & \text{for } r \leq 3\alpha_0, \end{cases}$$

where $f = \exp[-5(r-3)^2]$. Equation (5) applies to both the $^2A'$ and the $^2A''$ PESs.

Contour plots of the $^2A''$ PES are shown in Fig. 6. The $^2A''$ PES is purely attractive at large $HN-H$ distances and the TS region towards linearity is wide as one can see in Fig. 6(b). Similar plots are depicted in Fig. 7 for the $^2A'$ PES. Because of the conical intersection of the $^2A'$ state with the second state of the same symmetry at small angles $\alpha$, a shallow second minimum is seen near $\alpha = 50^\circ$ in Fig. 7(b). The main minimum is very shallow toward the linear H–N–H geometry; the barrier to linearity on the $^2A'$ PES is only $1.981$ kcal/mol. For long $HN-H$ distances the ground-state PES is more attractive than the excited-state PES, as demonstrated in Fig. 8, where we show the energies along the minimum-energy paths for both states. The different attractions of both PESs will have consequences for the corresponding reaction cross sections.

### C. Calculation of bound states

In order to assess the accuracy of the ground-state PES—apart from equilibrium geometries and dissociation energies—we calculate the low-lying vibrational energies for total nuclear angular momentum $J=0$ and compare them with the experimental transition energies. A complete theoretical description should take into account the electronic angular momentum, i.e., the RT coupling between the $^2A''$ and $^2A'$ states. Such calculations have been performed for NH$_3$ by, for example, Gabriel et al.$^7$ These authors have used ab initio PESs, which were modified, however, by a least-squares procedure to reproduce the experimental data with

<table>
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<th>$i$</th>
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<th>$E$</th>
<th>Expt.-calc.$^a$</th>
<th>$i$</th>
<th>$(v_1,v_2,v_3)$</th>
<th>$E$</th>
<th>Expt.-calc.$^a$</th>
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<td>10 978.1</td>
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$^a$Experimental transition energies taken from Table 6 in Ref. 7.
The three harmonic frequencies
s
g
diagonalization method 30,31 is used to determine the vibra-
tion of high quality. In summary, both PESs are
used above for describing the N + H 2 channel. The filter
data, as given in Table VI of Ref. 7. The agreement is very
good, except for the high bending states
high precision. A complete description of the spectroscopy of
NH 2 is beyond the purpose of the present investigation.
Here, we consider only the low-lying vibrational states of the
system with 160 Gauss Legendre points. Points on this grid
are listed in Table V and compared with experimental
data, as functions of temperature.

<table>
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<th>ND(X s 3Σ −)+H(3S)→</th>
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<td>3.7(13) s</td>
<td>6.4 (11)</td>
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<tr>
<td>300</td>
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<td>4.1 (13)</td>
<td>1.2 (12)</td>
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<td>4.3 (13)</td>
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<tr>
<td>500</td>
<td>4.5 (13)</td>
<td>2.3 (12)</td>
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<tr>
<td>700</td>
<td>4.7 (13)</td>
<td>4.0 (12)</td>
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<tr>
<td>900</td>
<td>4.8 (13)</td>
<td>5.8 (12)</td>
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</table>

*Numbers in parentheses indicate powers of ten.

The calculations of the bound states are performed using
the Jacobi coordinates appropriate for the NH–H channel:
R’, the distance from H to the center of mass of NH; r’, the
NH bond length; and y’, the vector between the vectors R’
and r’. Note, these Jacobi coordinates are different from the
ones used above for describing the N+H 2 channel. The filter
diagonalization method30,31 is used to determine the vibra-
tional energy levels and wave functions. The Hamiltonian
is evaluated by a three-dimensional discrete variable represen-
tation (DVR).32 The DVR grid in R’ ranges from 1.4 to 4.0a 0
with 80 grid points, the grid in r’ ranges from 0.9 to 4.0a 0
also with 80 DVR points, and y’ is varied between 0 and
180° with 160 Gauss Legendre points. Points on this grid
with an energy of 3.5 eV above the minimum are discarded.

The first 40 vibrational transition energies for the 2A”
state are listed in Table V and compared with experimental
data, as given in Table VI of Ref. 7. The agreement is very
good, except for the high bending states (0,7,0) and (0,8,0).
The latter two states lie well above the barrier for linearity
(1.46 eV above equilibrium) and therefore a model without
RT coupling is not appropriate.

A similar study for the excited state without RT coupling
to the ground state is not meaningful. Therefore, only a
harmonic analysis is performed in the minimum of the 2A’ PES.
The three harmonic frequencies (in cm−1) are 977.6 (964),
3619.2 (3635), and 3931.3 (3953). They agree well with the
harmonic frequencies for the 2A” state of Gabriel et al.1 (val-
ues in parentheses), which have been fitted to reproduce the
experimental transition energies. In summary, both PESs are
of high quality.

IV. TRAJECTORY CALCULATIONS

Cross sections for reactions (1a) and (1b) are calculated by
classical trajectories as functions of the collision energy
Ec and the initial rotational quantum number j of NH as indicated.
Calculated using the 2A” potential energy surface of this work.
The initial rotational state is varied up to 40 kcal/mol for reaction
(1a) and up to 15 kcal/mol for reaction (1b). The initial
rotational state is varied up to j = 20 in both cases. The
internal energy of NH is initially set to the quantum-
mechanical zero-point energy for a particular state (ν=0,j).
The maximum impact parameter is separately adjusted for
each collision energy. For each E c and j, typically 10 000
trajectories are calculated.

The results of the cross-section calculations are depicted in
Fig. 9. The cross sections for reaction (1b) are, of course,
very similar to the results in paper I for the reaction
NH(X 3Σ −)+H(3S)→N(4S)+H 2(X 1Σ +). Because there is a
barrier in the reactant channel, the cross sections show a
pronounced threshold behavior and a sizable j dependence.
However, for a given Ec and j the cross sections for D as
collision partner are larger than for H atoms colliding with
NH (see Fig. 5 in paper I). A possible reason is that, because
of the smaller relative velocity for NH+D, the reactants are
more effectively funneled through the narrow TS near linear N–H–D, respectively, N–H–H arrangements. The cross sections for the isotope exchange reaction (1a) proceeding on the $^4\Sigma^+$ PES [lower part of Fig. 9(b)] are much smaller than the cross sections for reaction (1b); they are of no importance for the depletion of NH($^3\Sigma^-$) and are not taken into account in the subsequent calculation of the rate coefficients.

The cross sections for reaction (1a) [Fig. 9(a)] monotonously decrease with the collision energy as it is expected for a wide TS with no barrier. In the intermediate energy regime the cross sections show a clear-cut $j$ dependence, i.e., initial rotation gradually decreases the reactivity. For very low and for higher energies this dependence is not so clear.

Temperature-dependent rate coefficients are calculated by

$$k(T) = \frac{\eta}{(\pi \mu)^{1/2}} \left( \frac{2}{k_B T} \right)^{3/2} Q^{1/2} \sum_j (2j+1) \exp(-E_{j\nu}/k_BT) \times \int_0^\infty E_c \sigma(E_c, \nu, j) \exp(-E_c/k_BT) dE_c, \quad (6)$$

where $\mu$ is the reduced mass for the reactant channel, $k_B$ is the Boltzmann constant, $Q$ is the vibrational-rotational partition function, and $E_{j\nu}$ is the energy of NH(X) in state ($\nu = 0, j$). The electronic degeneracy factor $\eta$ is taken as 1/3 and 2/3 for reactions (1a) and (1b), respectively. These degeneracy factors reflect the spin multiplicities of the $^2\Sigma^+$ and $^4\Sigma^+$ states via which reactions (1a) and (1b) proceed.

Rate coefficients for reactions (1a) and (1b) are calculated in the range 250–1000 K (Fig. 9 and Table VI). $k_{1a}$ is of the order of $(4-5) \times 10^{13}$ cm$^3$ mol$^{-1}$ s$^{-1}$ and shows a very small positive temperature dependence. The rate coefficient for reaction (1b), on the other hand, is much smaller and therefore the total rate coefficient $k_{1} = k_{1a} + k_{1b}$ is mainly determined by $k_{1a}$. Because of its strong positive temperature dependence, however, the relative contribution of $k_{1b}$ slightly increases with temperature. Interestingly, the rate coefficient for reaction (1b) is roughly the same as the rate coefficient for the reaction NH($^3\Sigma^-$) + H($^2S$) $\rightarrow$ N($^4S$) + H$_2$(X$^1\Sigma^+_g$) calculated in paper I. The decrease of the prefactor due to $\mu^{-1/2}$ in Eq. (6) by a factor of approximately 0.7 for D atoms is compensated by an increase of the reaction cross sections as discussed above.

The calculated rate coefficient at room temperature for reaction (1) is $k_1 = 4.1 \times 10^{13}$ cm$^3$ mol$^{-1}$ s$^{-1}$. It is in very good agreement with the measured value of $k_1 = (3.9 \pm 1.5) \times 10^{13}$ cm$^3$ mol$^{-1}$ s$^{-1}$.

In order to get a better understanding of the dynamics of reaction (1a) we calculate not only the cross section for the isotope exchange reaction ($\sigma_{\text{reac}}$) but also the cross section for the formation of a NH$_2$(X$^1\Sigma^+_g$) complex ($\sigma_{\text{comp}}$). When D and NH approach each other on the $^3\Sigma^+$-state PES they experience a strong attraction and first form a highly excited complex. We define that a complex is created when the potential energy along a trajectory falls below a certain value $\tilde{V}(\tilde{X})$; in the present application we choose $\tilde{V}(\tilde{X}) = -1.25$ eV (which is 3 eV above the potential minimum). If energy were completely randomized among all degrees of freedom, one would expect that the complex breaks apart into the two identical product channels NH+D and ND+H with equal probability. The consequence would be that the reaction cross section $\sigma_{\text{reac}}$ is approximately half the complex formation cross section $\sigma_{\text{comp}}$. This is, however, not the case as illustrated in Fig. 11(b). The ratio $P = \sigma_{\text{reac}}/\sigma_{\text{comp}}$ is significantly smaller than 0.5 for all the three possible isotope com-
The reactant and product channels of the H + NH reaction is more statistical at low collision energies but is significantly slower as observed experimentally in reaction (2). The ratio of the reaction paths in reaction (1) leading to the depletion of NH(X) or recovery of NH(X), which is obtained from the trajectory calculations, it can be concluded that the high-pressure limit of the rate coefficient of reaction (1) is of the order of \( k_1(\infty) = 1.6 \times 10^{-13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \).

The experimental data of the equilibrium geometries, dissociation energies, and the \( 2\text{A}''/2\text{A}' \) separation are well described by the two global PESs for the \( 2\text{A}'' \) and \( 2\text{A}' \) states of NH$_2$ constructed by ab initio calculations (MRCI, full-valence CASSCF wave functions, and aug-cc-pvqz basis set). Furthermore, the calculated vibrational transition energies in the electronic ground state are in very good agreement with the experimental energies.

Cross sections for reactions (1a) and (1b) have been calculated by classical trajectories over wide ranges of the collision energy and the initial rotational state. In accordance with a barrierless PES and a wide transition state, the reaction cross section for the \( 2\text{A}'' \) state decreases with increasing collision energy. In contrast, the cross section for reactions proceeding on the \( 2\text{A}' \) PES increases with energy, in agreement with a reaction barrier and a linear transition state.

The calculated rate coefficient for reaction (1) is in good agreement with the measured one. The contribution of reaction (1b) at room temperature is only 2%. The good agreement with the measured rate coefficient indicates that Renner–Tenner coupling between the \( 2\text{A}'' \) and \( 2\text{A}' \) states is unimportant for reaction (1).

Despite the more than 4 eV deep potential well of the \( 2\text{A}' \) PES, the reaction dynamics is not statistical. The temporarily formed NH$_2$(X)$^\dagger$ complex preferentially decays to the educt channel, i.e., energy redistribution is far from complete. The nonstatistical effect depends markedly on the isotope combination.

The authors are grateful to Professor J. Troe for stimulating interest and financial support. They also thank Professor P. Rosmus for performing the harmonic analysis for the \( 2\text{A}' \) potential energy surface. Financial support from the Fonds der Chemischen Industrie is acknowledged.

**ACKNOWLEDGMENTS**

We have measured, for the first time, the consumption of NH(X) radicals in reactions with D atoms, i.e., NH(X) +D(2S)→products (1). The measured rate coefficient at room temperature is \( k_1 = (3.9 \pm 1.5) \times 10^{-13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \). Comparing this value with the rate coefficient obtained for NH(X) +H(2S)→products (2) it can be concluded that reaction (1) is mainly determined by the H/D exchange reaction, which has to occur on the \( 2\text{A}' \) ground state potential energy surface (PES). The other possible reaction channel, i.e., the production of N(\( ^4\text{S} \)) atoms, is significantly slower as observed experimentally in reaction (2). From the ratio of the reaction paths in reaction (1) leading to the depletion of NH(X) or recovery of NH(X), which is obtained from the trajectory calculations, it can be concluded that the high-pressure limit of the rate coefficient of reaction (1) is of the order of \( k_1(\infty) = 1.6 \times 10^{-13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \).
The reactions $\text{NH}(X^3\Sigma_-^\text{o}) + \text{D}^1(S) \rightarrow \text{ND}(X^3\Sigma_-^\text{o}) + \text{H}^1(S)$


(2002).

23 H.-J. Werner, P. J. Knowles, R. Lindh et al., MOLPRO, version 2002.6, a package of ab initio programs (2003); see http://www.molpro.net.
26 The thermodynamical data for $\Delta H$ (in kcal/mol) from Ref. 27 are 84.0 for NH, 52.1 for H, 112.9 for N, 0.0 for $H_2$, and 44.19 for $NH_2$.