

Highly selective Si_3N_4/SiO_2 etching using an $NF_3/N_2/O_2/H_2$ remote plasma. I. Plasma source and critical fluxes

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ABSTRACT

Highly selective plasma etching of silicon nitride (Si_3N_4) , while not etching silicon dioxide (SiO_2) , is a critical step in the fabrication of microelectronics devices. In many applications, this etching must be damage-free and isotropic, which then motivates the use of remote plasmas where the reactants interacting with the substrate are dominantly neutral species. In this paper and Paper II, mechanisms for highly selective Si_3N_4 etching in remote plasmas are discussed based on results from experiments and simulations. It has been shown experimentally that high Si_3N_4/SiO_2 etch selectivity (≈ 380) can be achieved in the downstream effluent of an NF₃/N₂/O₂/H₂ plasma. The authors found that H₂ plays a principal role in the reaction mechanism as Si_3N_4/SiO_2 selectivity shows a sharp maximum as a function of the H₂ flow rate. Based on this observation, and measured densities of F-atoms and H₂ in the process chamber, a mechanism for NF₃/N₂/O₂/H₂ plasmas and its afterglow was developed to computationally determine the species densities and fluxes on the wafer level, validated by comparing with experimentally measured F-atom and H₂ densities. The calculated species densities and fluxes were used as input to an analytical model of Si_3N_4 and SiO_2 etching based on the results of quantum chemistry simulations. This paper presents experimental results (etching data and species densities), the reaction mechanism for NF₃/N₂/O₂/H₂ plasmas, and the results of simulations of elementary etching reactions, description of the analytical model of Si_3N_4 and SiO_2 etching based on the results of quantum chemistry simulations. This paper presents experimental results (etching data and species densities), the reaction mechanism for NF₃/N₂/O₂/H₂ plasmas, and the results of simulations of gas phase chemistry. Quantum chemistry simulations of elementary etching reactions, description of the analytical model of Si_3N_4 and SiO_2 selectivity with this model are

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I. INTRODUCTION

Plasma etching and cleaning are critical processes used in semiconductor fabrication.¹ These processes usually involve the direct contact of the plasma with the wafer, leading to ion bombardment that is necessary for producing anisotropic features, such as high aspect ratio vias and trenches. However, ion bombardment can produce defects in etched crystalline materials,^{1,2} and such defects become more of a concern as critical dimensions decrease. There is another class of etching processes requiring isotropic etching and extremely high selectivity, for example, etch selectivity of Si_3N_4 compared to SiO_2 of over 100. Isotropic high selectivity etching is difficult to achieve in conventional plasma sources. An alternative strategy for isotropic, selective, and nearly damage-free etching is to employ a plasma source that delivers only neutral radicals to the wafer.^{3–5} These radical fluxes can be produced by a remote plasma source (RPS), in which flow distance or the use of grids largely eliminates ion fluxes and delivers neutral radicals into the process chamber where the wafer is placed. Etching by neutral radicals without ions enables one to



achieve high etch selectivity⁶ for the proper choice of the process conditions (i.e., gas mixture, pressure, and RPS power).

It was earlier shown that high Si_3N_4/SiO_2 selectivity can be obtained with an RPS using gas mixtures such as $CF_4/N_2/O_2$ or $NF_3/N_2/O_2$.^{5,6} In our previous work,⁷ an RPS sustained in an NF_3/O_2 mixture achieved Si_3N_4/SiO_2 selectivity of about 80. Although an encouraging result, current fabrication processes require higher selectivity. Through optimization studies, selectivity was somewhat improved using NF_3/O_2 or $NF_3/N_2/O_2$ mixtures. At the same time, we have found that adding H_2 to $NF_3/N_2/O_2$ mixtures enables $Si_3N_4/$ SiO_2 selectivity of about 400. In these studies, Si_3N_4/SiO_2 selectivity showed a sharp maximum as a function of H_2 flow rate (FR), giving an indication of the importance of H_2 in the mechanism.

To investigate the role of H₂ in NF₃/N₂/O₂/H₂ mixtures in achieving high Si₃N₄/SiO₂ selectivity, we conducted experiments, plasma chemistry simulations, and etch process simulations (including quantum chemistry modeling of elementary etching reactions). After developing a reaction mechanism for NF₃/N₂/O₂/H₂ plasmas, comparisons were made to measurements of F-atom and H₂ densities above the wafer. Good correlation of simulations with experimental data as a function of the H₂ flow rate enabled us to propose a new mechanism for selective Si₃N₄/SiO₂ etching.

The new mechanism proposes an important role for HF molecules in vibrationally excited states to accelerating some etching reactions. The mechanism was incorporated into an analytical model of Si_3N_4 and SiO_2 etching, which uses the calculated species densities and fluxes as input. The analytical model is based on the results of quantum chemistry modeling of elementary etching reactions. The combined modeling hierarchy reproduces experimental trends and, in particular, the sharp maximum of Si_3N_4/SiO_2 selectivity versus H_2 flow rate.

This paper presents experimental results (etching data and species densities at the wafer level), a description of the reaction mechanism for NF₃/N₂/O₂/H₂ plasmas and results of simulations of gas phase chemistry in different parts of the remote plasma etching system using this reaction mechanism. Quantum chemistry simulations of elementary etching reactions, description of the analytical model of Si₃N₄ and SiO₂ etching, and calculations of the etch rates and Si₃N₄/SiO₂ selectivity are presented in Paper II.⁸

II. REMOTE PLASMA SOURCES FOR SELECTIVE ETCHING

A. Experimental setup and diagnostics

The remote plasma etching system used in this study is called the damage-free etcher (DFE) since it enables one to minimize defects in etched structures due to ion bombardment. The DFE is schematically shown in Fig. 1. The system design is similar to that used in our previous study,⁷ with the main difference being that we use two identical RPSs rather than one. The RPS is a capacitively coupled plasma (CCP) source of proprietary design operating at 60 MHz. Using two RPSs provides independent control of radical production. That is, generation of different radicals can be separately optimized. Another important feature of the DFE is the gas mixing cavity with a showerhead, which separates the cavity from the process chamber. Both RPSs are connected to the cavity with manifolds. The gas mixing



FIG. 1. Schematic of the DFE.

cavity and the showerhead provide uniform radical transport from both RPSs into the process chamber.

The DFE is equipped with optical emission spectroscopy (OES) diagnostics. A spectrometer receives optical emission from a viewport looking inside the process chamber via an optical fiber. Under normal operating conditions, there was no plasma in the process chamber, as indicated by the absence of optical emission. To provide excitation (and so optical emission) of the species in the process chamber, a low density plasma was produced by applying a low power (≤30 W) radio frequency (RF) bias at 13.56 MHz to the electrostatic chuck. The resulting emission enabled, for example, measurement of the F-atom density over the wafer by actinometry.⁹⁻¹¹ We confirmed that this low density plasma makes only a small contribution to F-atom generation and that the main source of F-atoms at the wafer level is the RPS. In addition to the OES diagnostics, a residual gas analyzer (RGA) mass-spectrometer was connected to the same viewport to measure H₂ densities in the process chamber.

Measuring F and H_2 densities in the process chamber as a function of the H_2 flow rate (FR) is important for validating the



gas phase chemistry simulations. The results of such measurements are shown in Fig. 2 for experimental conditions close to those used for our etching process, the main difference being adding 100 sccm of Ar for actinometry. The experimental conditions were as follows:

- RPS1: NF₃/Ar/N₂/O₂ = 10/100/150/200 sccm; RF power = 1000 W;
- RPS2: O₂ = 400 sccm, RF power = 2000 W;
- Manifold-2: 0-90 sccm H₂; and
- Process chamber: 350 mTorr; RF bias power (13.56 MHz) = 25 W.

 ${\rm H}_2$ was injected into manifold-2 close to its entry into the gas mixing cavity.

The F-atom density was determined by actinometry in the same manner as our previous studies.⁷ The radical number density [R] is obtained from

$$[R] = C_{Ar}^{R} * \frac{I(R)}{I(Ar)} * [Ar], \qquad (1)$$

where I(R) and I(Ar) are the radical and Ar-line emission intensities, respectively, and [Ar] is the density of the actinometer species Ar in plasma. Here, C_{Ar}^{R} is the actinometric coefficient, ^{12–15} which is a function of the plasma parameters (electron temperature or electron energy distribution, EED). For Eq. (1) to be valid, the emitting states of the radical and actinometer species should be populated mainly by electron impact excitation from the ground state and should dominantly decay by photon emission. Also, the emitting states of the radical and actinometer should have similar threshold energies and similar shapes of the cross sections for electron impact excitation. These conditions are fulfilled quite well for F-atom emission at 704 nm ($3p^2P^{\circ} \rightarrow 3s^2P$) and Ar emission at 750 nm ($4p'[1/2] \rightarrow 4s'[1/2]^{\circ}$). For these transitions, the actinometric coefficient



FIG. 2. Measured F-atom and $\rm H_2$ densities in the process chamber as a function of $\rm H_2$ flow rate.

 C_{Ar}^F is nearly constant over a wide range of plasma parameters and is a weak function of the shape of the EED.¹⁵ Thus the actinometric coefficient value $C_{Ar}^F \approx 2.0$ from 15 was used for determining absolute F-atom number densities.

As shown in Fig. 2, the densities of F-atoms and H₂ have complementary dependence on H₂ FR in the process recipe. At low H₂ FR, [F] has a monotonic decrease with increasing H₂ FR. However, at H₂ FR \geq 20 sccm, the decrease in [F] accelerates. Within an increase of 2 sccm of H₂ FR, the F-atom density decreases below the sensitivity of the OES measurements (\approx 10¹⁰ cm⁻³). [F] then remains at this low level for all higher values of H₂ FR (22–90 sccm). At the same time, the H₂ density measured with the RGA has the opposite trend. At low H₂ FR (0–20 sccm), [H₂] has a mild increase followed by a sharper increase at H₂ FR \geq 20 sccm. At H₂ FR (\geq 40 sccm), there is a milder increase in [H₂]. The sharp decrease of [F] and the sharp increase of [H₂] take place at nearly the same values of H₂ FR—the F-atom and H₂ densities in the process chamber are strongly coupled.¹⁶

B. Etching data

Blanket etching of Si₃N₄ and SiO₂ was peformed using the DFE plasma source. We started the investigation with a continuous etching process and found that when using NF₃/N₂/O₂/H₂ mixtures, the Si₃N₄ etch rate decreased with time. In some cases, the etching stopped. The slowing in the etch rate did not occur for SiO₂. The decrease in Si₃N₄ etch rate, as well as the etch stop, could be explained by the formation of a solid byproduct on the Si₃N₄ surface, most likely ammonium hexafluorosilicate, (NH₄)₂SiF₆, as previously proposed by several groups.^{17–23} SEM analysis of the surfaces confirmed that the SiO₂ surface was clean, whereas the Si₃N₄ surface had a solid byproduct.

To avoid the decrease in Si_3N_4 etch rate and the etch stop, we applied a cyclic etching process consisting of three steps: etching, annealing, and cooling. The RPSs were only operated during the etch step. After the etch step, the samples were transferred into the annealing chamber through a vacuum transfer system to avoid contact with the atmosphere. The samples were then heated to 200 °C for 60 s in pure Ar at a pressure of 2 Torr and a flow rate of 2000 sccm. After annealing, the hot samples were transferred back into the etching chamber and cooled to room temperature. The next etching step then commenced.

The cyclic etching process was used for both Si_3N_4 and SiO_2 so that a side-by-side comparison of etching the materials could be made. All conditions for Si_3N_4 and SiO_2 were the same except for the length of the etch step. The length of the etch step for SiO_2 was 600 s. However, since the etch rate of Si_3N_4 for some recipes was much higher than that of SiO_2 , the etch step time was 20 s for Si_3N_4 . The 20 s was the minimum time required to obtain stable plasma conditions in both RPSs, an important consideration to reproduce the etching results. For SiO_2 , the plasma on-time time was long enough to produce more than 100 A of total etch amount during the cyclic etching process consisting of up to 100 cycles. The total etch amount for Si_3N_4 was 300–2500 A for the cyclic etching process.

The etch rates were measured using blanket Si_3N_4 and SiO_2 coupons (4 × 4 cm²) deposited on silicon substrates. Si_3N_4 films were



produced by low-pressure chemical vapor deposition, and SiO_2 films were produced by thermal oxidation. The change in the film thickness was measured using a K-MAC ST5000 noncontact reflectometer. Etch rates and selectivity have an accuracy of about 10%.

 Si_3N_4 and SiO_2 etch rates, and Si_3N_4/SiO_2 selectivity are shown in Fig. 3 for $NF_3/N_2/O_2/H_2$ gas mixtures for two process recipes. In both the recipes, all process parameters were fixed and only the flowrate of H_2 was varied. In the first recipe [Fig. 3(a)], the process conditions were as follows:

RPS1: NF₃/N₂/O₂ = 15/150/250 sccm; RF power = 1000 W and
 RPS2: O₂ = 400 sccm, RF power = 2000W; manifold-2:
 20-50 sccm H₂.

The process conditions of the second recipe [Fig. 3(b)] almost coincide with those of Fig. 2, and the main difference being the absence of Ar in the recipe. The data are shown as a function of



FIG. 3. Measured Si_3N_4 and SiO_2 etch rates, and Si_3N_4/SiO_2 selectivity as a function of (a) H_2/NF_3 ratio and (b) H_2 flow rate.

the H₂:NF₃ ratio in the recipe [Fig. 3(a)], or as a function of H₂ FR [Fig. 3(b)].

For the data presented in Fig. 3(a), both Si₃N₄ etch rate and Si₃N₄/SiO₂ selectivity show strong variation with a pronounced maximum as a function of H₂ FR. Note that the highest Si₃N₄/SiO₂ selectivity, of about 130, exceeds the maximum selectivity of 80 when using NF₃/O₂ process gas.⁷ With other process parameters, a higher selectivity of about 380 was achieved [Fig. 3(b)]. The Si₃N₄/SiO₂ selectivity shown in Fig. 3(b) has a sharp peak versus H_2 FR, decreasing by roughly three times from the peak when the H₂ FR changes by only 1 sccm, while the total gas flow rate is about 800 sccm. Such variation of selectivity with H₂ FR should have a clear physical origin, for example, the radical responsible for selective Si₃N₄ etching should also have a sharp peak versus H₂ FR. However, the measured (Fig. 2) and initially simulated (see below) densities of the assumed relevant radicals in the process chamber on the wafer level do not show such behavior. Therefore, the peak of Si₃N₄/SiO₂ selectivity (Fig. 3) is likely the result of a species not conventionally categorized as an etch precursor.

C. HF(v) hypothesis

After considering several options, we hypothesized that the species responsible for the high measured Si_3N_4/SiO_2 selectivity is HF(v), vibrationally excited HF. The internal energy of HF(v) can be utilized for overcoming the activation barrier in etching reactions, resulting in HF(v) being more reactive than HF in the ground vibrational state. The vibrational quantum of HF(v) is 0.49 eV. Given the reaction mechanism, if this is the precursor species, the density of HF(v = 1) should have a peak as a function of H₂ FR.

HF is generated in the fast exothermal reaction,

$$F + H_2 \rightarrow HF(v) + H.$$
 (2)

As discussed in Sec. III, HF(v > 0) species are produced with a high branching ratio. HF(v > 0) is transformed into HF(v = 0) either by emitting an infrared photon,

$$HF(v = n) \rightarrow HF(v = n - 1) + hv, \tag{3}$$

or by collisional quenching,

$$HF(v = n) + M \rightarrow HF(v = n - 1) + M, \tag{4}$$

where M is a heavy neutral species (molecule or radical). Note that H_2 has a vibrational quantum (0.52 eV) close to that of HF (0.49 eV).¹⁵ For this reason, the collisional quenching of the first excited state

$$HF(v = 1) + H_2(v = 0) \rightarrow HF(v = 0) + H_2(v = 1)$$
 (5)

is a quasiresonant process and thus is rather fast. HF(v = 1) should be the most important source of excitation energy to the wafer in the etching chemistry, since it is the most abundant vibrationally excited species while having a comparatively long lifetime with respect to radiative de-excitation. So, in the following discussion, we consider only the first vibrationally excited state HF(v = 1).



The expected dependence of HF(v = 1) density as a function of H₂ FR is shown in Fig. 4. The initial increase of [HF(v = 1)] with H₂ FR is due to the increase in HF production by reaction (2), while the following decrease is due to quasiresonant quenching in reaction (5) at high H₂ density.

Reaction (2) enables one to qualitatively explain the behavior of F-atom and H₂ densities as a function of H₂ FR shown in Fig. 2. HF is a stable molecule, which is not dissociated in the process chamber in the absence of plasma—it is a terminal species that is pumped out. With reaction (2) being the main process for consuming F-atoms, increasing H₂ FR leads to a decrease of [F] in the process chamber. Much like a titration experiment, increasing H₂ FR will eventually consume all of the available F-atoms, capturing them in stable and unreactive HF molecules. This will take place at H₂ FR corresponding to the condition [F] \approx [H₂], where [F] and [H₂] are the species densities in the process chamber. For all higher H₂ FR, F-atoms in the process chamber will be similarly consumed, which is consistent with the measurements (Fig. 2).

The behavior of H₂ density versus H₂ FR can be explained in a similar manner. At low H₂ FR values, the F-atom density is high, which consumes injected H₂, thereby reducing the H₂ density. As long as the available F-atoms exceed the inventory of H₂ in making HF, the H₂ density only marginally increases with H₂ FR. At the point that the H₂ FR matches the production of F-atoms, that is, [F] \approx [H₂], the formation of HF will have depleted the inventory of F-atoms, after which the H₂ density should increase with H₂ FR. This is the trend that is observed experimentally (Fig. 2).

The H_2 FR at which $[F] \approx [H_2]$ should also correspond to the maximum of [HF(v=1)]. Indeed, at lower FR, HF(v=1)



FIG. 4. Schematic of variation of HF(v1) density vs H₂ flow rate.

production is low, while at higher FR, the quenching in reaction (5) decreases [HF(v = 1)]. Finally, if HF(v = 1) plays an important role in Si₃N₄/SiO₂ selective etching, the condition [F] \approx [H₂] may be a condition for achieving the maximum etch selectivity.

III. GAS PHASE PLASMA CHEMISTRY SIMULATIONS

A. Description of the models

Two simulation techniques were used to model DFE—a global model using a plug-flow approximation to address plasma and radical generation and a 2D model combining fluid and kinetic approaches to address flow and electron kinetics. We used the global model in order to study the variation of radical densities when changing the process recipe over the full range of the process conditions. The 2D model was used to determine the power into electrons—an important parameter for the global model input.

The global model, Global-Kin, is a 0-dimensional simulation for plasma chemistry, plasma kinetics, and surface chemistry.²⁴ The global model is implemented in a plug-flow mode whereby integration in time is mapped to integration in space by computing a time dependent flow speed. Assuming a constant pressure, the flow speed is determined by the input flow rate, dimensions of the reactor, and the thermal expansion (or contraction) of the gas due to changes in temperature and changes in gas number density due to electron impact and neutral reactions, limited by requiring the flow to be subsonic. The global model consists of differential equations for the densities of species based on the defined reaction mechanism. The power deposition is specified as a function of position.

With electron impact cross sections and mole fractions of gas species, Boltzmann's equation is solved for EEDs over a wide range of E/N (E and N are the electric field and the gas number density) and so the non-Maxwellian nature of the EEDs is addressed.²⁵ This process produces a table of E/N, average electron energy (or equivalent electron temperature, T_e), and electron impact rate coefficients. If T_e is a monotonic function of E/N, the lookup table can be interpolated for rate coefficients as a function of T_e , $k_i(T_e)$, where the instantaneous T_e is produced by the electron energy equation. The table is periodically updated as mole fractions of species change.

More system specific issues of the downstream etch system were investigated using 2D modeling with the Hybrid Plasma Equipment Model (HPEM).²⁶ The HPEM is a modular simulator that combines fluid and kinetic approaches. In the HPEM, continuity, momentum, and energy equations for all species are solved coincident with Poisson's equation for the electric potential. The use of the HPEM explicitly calculates all modes of power (electron and ion) self-consistently. Electron transport is addressed using fluid equations for bulk electrons and a kinetic Monte Carlo simulation for sheath accelerated secondary electrons, which play an important role in the electron heating mechanism in capacitively coupled plasmas. The same procedure is followed to obtain electron impact rate coefficients for the fluid electrons as described for the global model. Nonlocal electron energy transport is accounted for through the thermal conductivity and convection terms of the electron energy equation that provide an electron temperature as a function of position.



B. Reaction mechanism for NF₃/O₂/H₂

A reaction mechanism was developed for plasmas sustained in gas mixtures initially containing NF₃/O₂/H₂. The same mechanism was used in both the global and 2D models. The species included in the model are listed in the Appendix. The rate coefficients for heavy particle collisions are listed in the Arrhenius form, while the rate coefficients for electron impact reactions were calculated based on the EEDs produced by solutions of Boltzmann's equation. The reactions that would occur in NF₃/O₂ mixtures are the same as discussed previously.²⁷ The additional reactions required to complete the mechanism for NF₃/O₂/H₂ mixtures are electron impact collisions with H₂, H, NH_x, HF, H_xO_y, and heavy particle reactions involving H atoms. These additional reactions are listed in the Appendix. The resulting reaction mechanism is intended to be as complete as practical for a discharge sustained in NF₃/N₂/O₂/H₂ mixtures. As such, there are rate coefficients whose values have not been experimentally or analytically determined, and so a subset of the reaction rate coefficients was estimated based on enthalpies of reactions and in analogy with similar reactions. For example, the rate coefficient for charge exchange between ions and neutrals was assumed to be 1×10^{-11} cm³ s⁻¹ (1×10^{-9} cm³ s⁻¹ for resonant charge exchange),28 and the rate coefficient for neutralization between positive and negative ions was assumed to be $2 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$

For plasmas sustained in NF_3/O_2 mixtures, the molecular gases are dissociated to form NF_2 , NF, F, and O by electron impact dissociative attachment and dissociative excitation,

$$e + NF_x \rightarrow NF_{x-1} + F^-$$
, $x = 1-3$, (6a)

$$e + NF_x \rightarrow NF_{x-1} + F + e, \tag{6b}$$

$$\mathbf{e} + \mathbf{O}_2 \to \mathbf{O} + \mathbf{O}^-,\tag{6c}$$

$$e + O_2 \rightarrow O + O + e. \tag{6d}$$

These reactions, proceeding through electronic dissociative states, produce translationally hot fragments through the Franck–Condon effect which contributes to gas heating. The resulting high gas temperatures then enable endothermic heavy particle reactions to occur. The reactions among the products of reactions in Eq. (6) and the background gases result in reactive N_xO_y species, which can be used as etchants for surface reactions or precursors for downstream reactions. In many RPS, the gas temperature significantly drops from the plasma zone to the downstream chamber, enabling opportunities to customize endothermic reactions have a positive change in enthalpy ($\Delta H > 0$), whereas exothermic reactions have a negative change in enthalpy ($\Delta H < 0$).

The formation of N_2O occurs through the endothermic reactions

$$N_2 + O_2 \rightarrow O + N_2O$$
, $\Delta H = 3.5 \text{ eV}$, (7a)

$$NO + NO \rightarrow O + N_2O$$
, $\Delta H = 1.7 \text{ eV}$, (7b)

and exothermic reaction

$$N + NO_2 \rightarrow O + N_2O$$
, $\Delta H = -1.7 \text{ eV}$. (7c)

The formation of NO occurs through endothermic reactions

$$N_2 + O \rightarrow N + NO$$
, $\Delta H = 3.2 \text{ eV}$, (8a)

$$N_2 + O_2 \rightarrow NO + NO, \quad \Delta H = 1.8 \text{ eV},$$
 (8b)

and exothermic reactions

$$N + O_2 \rightarrow NO + O, \quad \Delta H = -1.4 \text{ eV},$$
 (8c)

$$N + NO_2 \rightarrow NO + NO, \quad \Delta H = -3.4 \text{ eV},$$
 (8d)

$$NO_2 + O \rightarrow O_2 + NO$$
, $\Delta H = -2.0 \text{ eV}$, (8e)

$$N_2O + O \rightarrow NO + NO, \quad \Delta H = -1.7 \text{ eV}.$$
 (8f)

These exothermic reactions are not inhibited by the decreased temperatures as the gas flows downstream and results in NO being the dominant radical entering the downstream region.

With the addition of H₂ downstream of the NF₃/N₂/O₂ plasma, reactions between H₂/H and the dominant downstream species (e.g., O, F, NF_x, and N_xO_y) lead to a variety of products mainly through exothermic reactions. For instance, HF molecules are formed through reactions which usually have an exothermicity larger than the vibrational quanta of HF (0.5 eV), resulting in the formation of vibrational states of HF, HF(v), through Eqs. 9(a)-9(f) from 30-35, respectively,

$$H + NF_2 \rightarrow NF + HF(v = 0, 1, 2, ...), 0.71/0.22/0.07,$$
 (9a)

$$H + F_2 \rightarrow F + HF(v = 0, 1, 2, ...), \quad 0.01/0.03/0.96,$$
 (9b)

$$F+H_2 \to H+HF(v=0,\,1,\,2,\,\ldots), ~~0/0.15/0.85, ~~(9c)$$

$$F+OH \to O+HF(v=0,\,1,\,2,\,\ldots), \quad 0.36/0.46/0.18, \qquad (9d)$$

$$F + H_2O \rightarrow OH + HF(v = 0, 1, 2, ...), \quad 0.21/0.75/0.04,$$
 (9e)

$$F + NH_3 \rightarrow NH_2 + HF(v = 0, 1, 2, \ldots), \quad 0.10/0.29/0.61, \ (9f)$$

where x/y/z following the reaction indicates the branching ratios for producing HF(v = 0), HF(v = 1), and HF(v ≥ 2). These reactions occur through the atomic H extracting an F-atom from the F-containing species or atomic F extracting H atom from the H-containing species to form HF, which has a high binding energy³⁶ of 5.9 eV and so is more stable than the reactant molecules.

There are additional exothermic reactions, which form HF,

$$H + NF_3 \rightarrow NF_2 + HF$$
, $\Delta H = -3.5 \text{ eV}$, (10a)



$$H + NF \rightarrow N + HF$$
, $\Delta H = -3.1 \text{ eV}$, (10b)

$$H + FO \rightarrow O + HF$$
, $\Delta H = -3.6 \text{ eV}$. (10c)

No branching ratios for forming HF(v) have been measured or calculated for these reactions according to available references. This may be due to the excess potential energy not being converted to vibrational energy but to other forms of kinetic energy (e.g., rotational energy and translational energy).

In addition to HF(v) being able to deliver energy to surfaces and contribute to surface reactions, HF(v) plays multiple roles in gas phase reactions including reducing activation energy as the vibrational level increases. For example, the endothermic reactions

$$\mathrm{HF} + \mathrm{F} \rightarrow \mathrm{F}_2 + \mathrm{H}, \quad \mathrm{E}_\mathrm{a} = 50\,640\,\mathrm{K}, \quad \Delta\mathrm{H} = 4.3\,\mathrm{eV}, \qquad (11a)$$

$$HF(v = 1) + F \to F_2 + H, \quad E_a = 44\,843\,K, \quad \Delta H = 3.8\,eV, \eqno(11b)$$

$$\mathrm{HF}(\mathrm{v}\geq2)+\mathrm{F}\rightarrow\mathrm{F}_{2}+\mathrm{H},\quad\mathrm{E}_{a}=39\,046\,\mathrm{K},\quad\Delta\mathrm{H}=3.3\,\mathrm{eV} \eqno(11c)$$

have reduced change in enthalpy and lower activation energy with the reactant HF increasing in the vibrational state. In exothermic reactions, the reactant HF(v) increases the exothermicity (thereby increasing gas heating), examples being,

$$HF + O^* \rightarrow OH + F, \quad \Delta H = -0.5 \text{ eV},$$
 (12a)

$$HF(v = 1) + O^* \rightarrow OH + F, \quad \Delta H = -1.0 \text{ eV},$$
 (12b)

$$HF(v \ge 2) + O^* \rightarrow OH + F, \quad \Delta H = -1.5 \text{ eV}.$$
 (12c)

In cases where reactions are marginally endothermic, $\mathrm{HF}(v)$ can convert endothermic reactions to exothermic reactions such as

$$\mathrm{HF} + \mathrm{OH} \rightarrow \mathrm{H}_2\mathrm{O} + \mathrm{F}, \quad \Delta\mathrm{H} = 0.7 \,\mathrm{eV}, \tag{13a}$$

$$HF(v=1)+OH \rightarrow H_2O+F, \quad \Delta H=0.2 \text{ eV}, \tag{13b}$$

$$HF(v \geq 2) + OH \rightarrow H_2O + F, \quad \Delta H = -0.3 \text{ eV}. \tag{13c}$$

HF(v) molecules can also transfer their vibrational quanta to other molecular species (e.g., H₂, N₂, O₂, and NH₃) through V-V processes

$$HF(v = 1) + H_2 \rightarrow HF + H_2(v = 1), \quad \Delta H = 0,$$
 (14a)

$$\mathrm{HF}(\mathrm{v}=1) + \mathrm{N}_2 \rightarrow \mathrm{HF} + \mathrm{N}_2(\mathrm{v}), \quad \Delta \mathrm{H} = -0.2 \, \mathrm{eV}, \qquad (14\mathrm{b})$$

$$HF(v = 1) + O_2 \rightarrow HF + O_2(v), \quad \Delta H = -0.3 \text{ eV}, \quad (14c)$$

$$HF(v = 1) + NH_3 \rightarrow HF + NH_3(v), \quad \Delta H = -0.1 \text{ eV}.$$
 (14d)

Similar to HF(v), these vibrational excited molecules can lower activation energies in reactions compared to their ground state molecules, favoring their reacting with other species in the downstream chamber.

In addition to being formed through reactions in Eqs. 9(e) and (12) $(F + H_2O \rightarrow OH + HF$ and $HF + O^* \rightarrow OH + F$), OH is also formed through the exothermic reactions

$$H + N_2O \rightarrow OH + N_2$$
, $\Delta H = -2.8 \text{ eV}$, (15a)

$$H + NO_2 \rightarrow OH + NO, \quad \Delta H = -1.3 \text{ eV},$$
 (15b)

$$H + FO \rightarrow OH + F$$
, $\Delta H = -2.2 \text{ eV}$, (15c)

and endothermic reactions

$$H_2 + O \rightarrow OH + H$$
, $\Delta H = 0.1 \text{ eV}$, (15d)

$$H + O_2 \rightarrow OH + O$$
, $\Delta H = 0.7 \text{ eV}$. (15e)

 $\rm H_2O$ molecules are mainly formed with OH as the precursors through reactions in Eq. (13) (HF + OH \rightarrow H_2O + F) and exothermic reactions

$$H_2 + OH \rightarrow H_2O + H$$
, $\Delta H = -0.6 \text{ eV}$, (16a)

$$OH + OH \rightarrow O + H_2O$$
, $\Delta H = -0.7 \text{ eV}$. (16b)

Small densities of ammonia species are formed in the downstream chamber due to the low gas temperature, which inhibits the endothermic reactions that form NH through

$$H_2 + N \rightarrow NH + H$$
, $\Delta H = 1.3 \text{ eV}$, (17a)

$$H + N_2 \rightarrow NH + N, \quad \Delta H = 6.5 \text{ eV}.$$
 (17b)

The resulting low densities of NH then limit the production of NH_2 and NH_3 through

$$NH + NH \rightarrow NH_2 + N$$
, $\Delta H = -0.9 \text{ eV}$, (17c)

$$H_2 + NH_2 \rightarrow H + NH_3$$
, $\Delta H = -0.2 \text{ eV}$. (17d)

C. Simulations with Global-Kin

When operated in a plug-flow mode, Global-Kin is able to address the flow plasma chemistry of the DFE, through the RPS, manifold, gas mixing cavity, and process chamber.²⁷ When using the plug-flow option, the DFE system is approximated by a series of cylinders as shown in Fig. 1. Simulations were carried out as follows. Gas flow and plasma chemistry through RPS1 + manifold-1 and RPS2 + manifold-2 were initially separately simulated based on their input gas streams. The fluxes and flow rates leaving these



sources were then used as the input parameters for the gas mixing cavity and the process chamber. To describe the gas flows from RPS1 and RPS2 into the gas mixing cavity and mixing of these two flows, we used two nozzles inside the cavity, as described below.

The specification of power in Global-Kin is essentially power deposition into electrons, akin to an inductively coupled plasma. The RPS1 and RPS2 are actually capacitively coupled plasmas (CCPs), whose power deposition is divided between electron heating and ion acceleration in the sheaths. To properly account for this division of power, HPEM simulations, which account for the division of power, were performed using the experimental geometry. The power deposition into ions and electrons was separately computed. The proportion dissipated by electrons was then used as input for Global-Kin simulations. For example, for the experimental conditions of Fig. 2, 1000 W of total power deposition corresponded to 600 W of electron power deposition, and this value was used in Global-Kin simulations. Note that this power deposition into electrons does not depend on H₂ FR, since H₂ is injected downstream of the RPS2 in manifold-2. Although some back diffusion of H₂ into the RPS likely occurs, this effect is not captured by plug-flow techniques.

Simulated electron and gas temperatures, as well as charged and neutral species densities, as a function of flow distance in RPS1 and manifold-1 are shown in Fig. 5. The gas mixture and flow rates are NF₃/Ar/N₂/O₂ = 10/100/150/200 sccm at a pressure of 700 mTorr, the same as in experiments, whose results are presented in Fig. 2. Here, x = 0 corresponds to the input gas nozzle, and $0 \le x \le 25$ cm corresponds to the RF power deposition zone (i.e., RPS1), while $25 \le x \le 45$ cm corresponds to manifold-1.

The electron temperature, T_e , shows a small peak at the start of the flow into RPS1, which is due to the rapid consumption of electrons to form negative ions F- through dissociative attachment to NF₃: $e + NF_3 \rightarrow F^- + NF_2$. A higher T_e is required to provide ionization to offset this loss of electrons and sustain the discharge. The fragments of NF₃ are less attaching, so as NF₃ is dissociated [see Fig. 5(d)], T_e decreases and the negative ion density drops to a lower value. The primary negative ion in the RPS1 plasma is F^- , while the main positive ion is NO⁺.

Outside the power deposition zone (i.e., in the manifold), T_e thermalizes to the gas temperature which occurs quickly at the relatively high gas pressures. The pressure in RPS1 was assumed to be 700 mTorr, while for the process chamber the pressure was 350 mTorr with the pressure differential occurring across the showerhead. The electron density drops to negligible values for $x \ge 25$ cm due to the low T_e (i.e., no electron impact ionization) and electron loss by thermal dissociative attachment dominantly to NF_x. As a result, in manifold-1 there is an ion-ion plasma,³⁷ characterized by nearly equal densities of positive and negative ions and



FIG. 5. Global modeling results for plasma properties as a function distance from the gas input of RPS1. (a) Electron temperature, (b) gas temperature, (c) charged species densities, and (d) neutral species densities. The flow rates are NF₃/Ar/N₂/O₂ = 10/100/ 150/200 sccm with a CCP power of 1000 W at 700 mTorr.



low electron densities. Although dissociative electron-ion recombination can occur, the low density of electrons results in there being little electron induced dissociation downstream of the plasma.

In passing through the plasma zone, molecular gases are strongly dissociated, particularly NF₃ and O₂ and to a lesser extent N₂. Thus, the neutral species leaving RPS1 are dominated by O, F and N atoms, and NO. Also, there are considerable amounts of FNO, F₂, and NO₂, which are byproducts of chemical reactions in the plasma volume. All these species (except N-atoms) survive in the manifold to reach the entrance of the gas mixing cavity.

Simulated electron and gas temperatures, as well as charged and neutral species densities, as a function of distance in RPS2 and manifold-2 are shown in Fig. 6 for an O₂ flow rate of 400 sccm. Here, the power into electrons for 2000 W of capacitive power was 1000 W for a gas pressure of 700 mTorr. The simulated T_e and T_g are lower than in RPS1, while the electron density is higher. Although O₂ is an electronegative gas, it is not a thermally attaching species and so the plasma can be sustained with lower T_e. The main positive ion in RPS2 is O⁺, while in the manifold-2 it is O₂⁺. Since O₂ and its fragments are not thermally attaching gases (at least at low pressure in the absence of three-body reactions), as T_e decreases in manifold-2, there is not a transition to an ion-ion plasma. The plasma retains its electropositive nature (n_e \approx [O₂⁺]). There is strong dissociation of O₂-molecules in RPS2 with $[O] \gg [O_2]$, resulting in the neutral flow at the exit of manifold-2 consisting mainly of O-atoms with a small fraction of O_2 molecules.

The gas flows from manifold-1 and manifold-2 enter into the gas mixing cavity. Simulated neutral species densities for two values of H_2 FR (5 and 50 sccm) are shown in Fig. 7 as a function of flow distance. Here, x = 0 and 3.2 cm correspond to the top and bottom of the gas mixing cavity. Note that the bottom coincides with the showerhead, which separates the gas mixing cavity and the process chamber.

To describe the gas mixing in the cavity, we employed two nozzles placed adjacent to each other. Nozzle-1 at x = 0 represents the gas flow from manifold-1, while nozzle-2 at x = 0.1 cm represents the gas flow from manifold-2. The gas flow through nozzle-1 consists of all species flowing out of manifold-1 in proportion to their mole fractions. Since H₂ is injected into manifold-2 close to the connection with the gas mixing cavity, we assumed that the gas flow through nozzle-2 consists of both the O and O₂ species produced by PRS2 as well as injected H₂. As consistent with the plug-flow approximation, we ignore the back diffusion of H₂ into manifold-2 and RPS2.

Simulated densities for the flow through the gas mixing cavity are shown in Fig. 7. The effect of H₂ injection enables the fast reaction (9c): $F + H_2 \rightarrow HF + H$. At low H₂ FR (5 sccm), [H₂] is



FIG. 6. Global modeling results for plasma properties as a function of distance from gas input of RPS2 of 400 sccm of O_2 for a CCP power of 2000 W. (a) Electron temperature, (b) gas temperature, (c) charged species densities, and (d) neutral species densities.

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FIG. 7. Simulated densities of neutral species in the gas mixing cavity as a function of distance: The densities shown in (a) and (b) are for H_2 FR = 5 sccm. The densities shown in (c) and (d) are for H_2 FR = 50 sccm.

nearly fully consumed by reaction with the more numerous F-atoms to form HF and H. In this process, F-atoms are consumed and the density decreases. However, since the initial $[H_2]$ is low, the fractional change in [F] is small. With a high H_2 FR (50 sccm), the situation is the opposite. [F] is essentially fully consumed by the higher flow of H_2 , while the fractional change in $[H_2]$ is small.

Downstream of the H₂ injection point, several reaction products are generated, including HF, HF(v), OH, and H₂O. The species HF(v) includes both HF(v = 1) and HF(v \geq 2), second and higher vibrational excited states. Upon H₂ injection, [HF] is generated by reaction with F-atoms produced upstream, increasing to a nearly constant value. At the same time, both [HF(v = 1)] and [HFv2] first increase and then decrease to steady-state values due to infrared emission and collisional quenching. Note that for high H₂ FR (50 sccm), the rate of collisional quenching is much greater due to the quasiresonant character of quenching with H₂.

OH and H₂O densities also show rapid increases after H₂ injection followed by rapid decreases to steady-state values. Note that for low H₂ FR (5 sccm), the steady-state density $[OH] \gg [H_2O]$, while for high H₂ FR (50 sccm), the relation is the

opposite, $[OH] \ll [H_2O]$. These results are a consequence of the fast reaction (16a), $OH + H_2 \rightarrow H_2O + H$, which depletes OH by the reaction of H_2 , producing H_2O .

Neutral species densities for the same values of H_2 FR (5 and 50 sccm) as a function of position in the process chamber are shown in Fig. 8. Here, x = 0 and 7.5 cm correspond to the top and bottom of the process chamber. Note that most of the species densities show only a weak variation with distance inside the process chamber, as the majority of the most reactive species have already been depleted in the plenum. The exceptions are OH, H_2O , and HF(v = 1), which continue to either react or be quenched in the process chamber. There are large differences in F, OH, and H_2O densities in the process chamber for low and high H_2 FR, which should imply differences in the etching results.

Simulated densities of the species that are most relevant to etching of Si_3N_4 and SiO_2 [F, H₂, O, H, NO, FNO, OH, H₂O, HF, and HF(v = 1)] in NF₃/N₂/O₂/H₂ mixtures in the process chamber at the wafer level (x = 7 cm) are shown in Fig. 9 as a function of H₂ FR. A common feature in the densities of these species is their dependence on flow rate around H₂ FR = 20 sccm, which is best demonstrated by the densities of F-atoms and H₂.





The simulated densities of F-atoms and H₂ at the wafer level are strongly correlated as a function of H₂ FR. This correlation is shown in Fig. 10. At low H₂ FR (<20 sccm), [F] has a monotonic decrease. Then, in a narrow range of H₂ FR (20–22 sccm), [F] quickly decreases from 5.7×10^{12} to 1.5×10^7 cm⁻³. After that transition, there is again a weak decrease, with [F] staying at a low level for the remaining range of H₂ FR (22–90 sccm). The behavior of H₂ is opposite to that of the F-atoms. Namely, [H₂] shows a moderately fast increase at low H₂ FR (<20 sccm), followed by a rapid increase in the same narrow range of H₂ FR (20–22 sccm), and then a slow increase for the remaining range of H₂ FR (22–90 sccm). The simulation results shown in Fig. 10 compare favorably with the experimental data presented in Fig. 2.

The transition point in [F] and [H₂] in the process chamber at an H₂ FR = 20 sccm, at which the relation [F] \approx [H₂] is fulfilled, mainly originates from the reaction F + H₂ \rightarrow HF + H. At low H₂ FR, the initial [F] \gg [H₂] so that all injected H₂-molecules are consumed by reactions with F-atoms produced upstream, generating HF and H. Thus, at lower flow rates than H₂ FR = 20 sccm, the F-atom density only slowly decreases and H₂ increases moderately fast with H₂ FR. When H₂ FR = 20 sccm is reached, [H₂] starts to increase with H₂ FR, since the density of F-atoms produced in the RPS is not sufficient to consume all of the injected H₂. For $[F] \ll [H_2]$, almost all F-atoms are consumed in the formation of HF corresponding to a low and slowly decreasing [F] and high and slowly increasing [H₂] with H₂ FR. The transition between these two regimes occurs over 20-22 sccm, while the total flow rate is of about 800 sccm. Such a narrow transition range could be something of an idealization in Global-Kin (which implies immediate mixing), while in reality the expectation is that the range should be wider. However, comparison with the experimental data (Fig. 2) shows that the transition does occur in a narrow range of H₂ flow rate. Note that the relation $[F] \approx [H_2]$ is fulfilled at an H₂ FR = 20 sccm only for these particular process conditions (i.e., geometry, gas mixture composition, RF powers in RPS1 and RPS2, and pressure). The qualification concerning the process conditions and system design is very important, since the H₂ FR value for which $[F] \approx [H_2]$ strongly depends on them.

Considering only reaction (9c) $F + H_2 \rightarrow HF + H$ to explain the behavior of F-atom and H₂ densities shown in Figs. 2 and 10 is something of a simplification. As follows from the reaction mechanism, F-atoms can also be consumed in other reactions producing HF [e.g., reactions (9d)–(9f)]. However, the rates of F-atom consumption in other reactions are much lower since the densities of OH, H₂O, and NH₃ are also much lower than that of H₂. Other consumption mechanisms, such as a



FIG. 9. Simulated densities of reactants in the process chamber at the wafer level as a function of H₂ flow rate for the same conditions as in Fig. 2: (a) O, H, NO; (b) F, H₂, H₂O, HF and (c) FNO, OH, HF(v=1).



FIG. 10. Simulated F-atom and H₂ densities in the process chamber as a function of H₂ flow rate for the same conditions as in Fig. 2.

series of reactions,

 $F + F(wall) \rightarrow F_2(volume), \quad H + F_2 \rightarrow HF + F,$ (18a)

$$F + O_3 \rightarrow FO + O_2$$
, $H + FO \rightarrow O + HF$, (18b)

make small contributions to the total F-atom consumption. The same is true for the H₂ density shown in Figs. 2 and 10, since for H₂ reaction (9c) is also the main consumption channel as long as F-atom density is sufficiently high (i.e., for H₂ FR < 20 sccm). Other channels, such as H₂ + O \rightarrow OH + H [reaction (15d)] and H₂ + OH \rightarrow H₂O + H [reaction (16a)], make much smaller contributions to the total H₂ consumption rate. As shown in Figs. 7 and 8, the reaction product HF density is much higher than the densities of products OH and H₂O.

The O-atom density [Fig. 9(a)] monotonically decreases with a change of the slope at H_2 FR = 20 sccm. The decrease with H_2 FR can be explained by the reactions

$$H_2 + O \rightarrow OH + H$$
, $\Delta H = 0.1 \text{ eV}$, (19a)

$$H + O_2 \rightarrow OH + O, \quad \Delta H = 0.7 \text{ eV}.$$
 (19b)

$$\label{eq:H2} H_2 + OH \rightarrow H_2O + H, \quad \Delta H = -0.6 \ \text{eV}, \tag{19c}$$

$$OH + OH \rightarrow O + H_2O$$
, $\Delta H = -0.7 \text{ eV}$. (19d)

These reactions overall consume O-atoms and produce stable H₂O. The rate of O-atom consumption increases with H₂ density and so with H₂ FR. The change of the slope results from the accelerated production of OH and H₂O because of the rapid increase of [H₂] at H₂ FR \geq 20 sccm [see Fig. 9(b)].



The H-atom density shows an almost linear increase with a slight change of the slope at H_2 FR = 20 sccm [Fig. 9(a)]. This behavior is explained by the reaction $F + H_2 \rightarrow HF + H$ [reaction (9c)], which is also the main mechanism of H-atom production. F-atoms are generated mainly in RPS1, so their flow into the mixing volume does not depend on H_2 FR. Since the rate of H-atom production is proportional to [H₂], the change of slope at H_2 FR = 20 sccm can be explained by the fast increase of [H₂] at H_2 FR \geq 20 sccm.

The NO density shows a weak monotonic decrease with H_2 FR [Fig. 9(a)]. NO is produced mainly in RPS1, so its density in the process chamber should not strongly depend on the H_2 FR. The weak decrease can be explained by dilution due to the added H_2 , which increases the total flow rate and so flow speed.

The density of FNO behaves similarly to that of F-atoms with a sharp decrease and minimum at H_2 FR = 20 sccm, followed by a slower increase and saturation at high H_2 FR [Fig. 9(c)]. The rapid decrease results from the reaction $F_2 + NO \rightarrow FNO + F$. The contribution of this reaction to FNO production decreases rapidly with H_2 flow rate around H_2 FR = 20 sccm, since [F₂] behaves similarly to [F], while [NO] weakly depends on H_2 FR. The slow increase of [FNO] at H_2 FR \geq 20 sccm is due to the reaction FNO + O \rightarrow F + NO₂, which is the main mechanism of FNO decay. The rate of this reaction decreases for H_2 FR \geq 20 sccm because the O-atom density decreases [Fig. 9(a)].

OH shows a monotonic increase with a change of the slope at H_2 FR = 20 sccm [Fig. 9(c)]. OH is produced in reactions (15a)–(15e). The monotonic increase of [OH] with H_2 FR is explained by the almost linear increase of [H] with H_2 FR, corresponding to reactions (15a)–(15c) and (15e). The change of the slope at H_2 FR = 20 sccm is explained by the rapid increase of [H₂] at H_2 FR ≥ 20 sccm, while the rate of reaction (15d) is proportional to [H₂].

The density of H_2O shows similar behavior as the density of H_2 with a rapid increase in the same range followed by a slower increase [Fig. 9(b)]. H_2O is produced in the reactions

$$HF + OH \rightarrow H_2O + F$$
, $\Delta H = 0.7 \, eV$, (20a)

$$H_2 + OH \rightarrow H_2O + H$$
, $\Delta H = -0.6 \text{ eV}$, (20b)

$$OH + OH \rightarrow O + H_2O$$
, $\Delta H = -0.7 \text{ eV}$. (20c)

This behavior indicates that the main channel of H_2O production for our conditions is reaction (20b).

HF shows a linear increase until H_2 FR = 20 sccm and a maximum followed by a slow decrease [Fig. 9(b)]. HF is produced in reactions (9a)–(9f). HF is not dissociated in the process chamber, making it a terminal species that is pumped out. The main production mechanisms for HF are reactions (9b) and (9c). Here, we do not distinguish HF and HF(v), since most of HF(v) become HF either by infrared emission or by collisional quenching. F-atoms are produced mainly in RPS1, so their flow into the mixing volume does not depend on H_2 FR, while the flow of F_2 is proportional to that of F and is much smaller. These trends explain the linear increase of [HF] with the H_2 flow rate until H_2 FR = 20 sccm. The slow decrease is explained by the combined effect of the fast decrease of [F] and an increase of [H₂] at H₂ FR \ge 20 sccm.

The simulated densities of H_2O and HF in the process chamber as a function of H_2 FR and the corresponding densities measured with the RGA are shown in Fig. 11. In both cases, the measured densities were normalized to the simulated values at H_2 FR = 90 sccm. There is qualitative agreement between the experimental and simulated results for densities of both H_2O and HF, lending credence to the reaction mechanism. At the same time, the differences between the experiments and simulations can be



FIG. 11. Experimental and simulated H_2O and HF densities in the process chamber as a function of H_2 flow rate: (a) H_2O and (b) HF.



explained by simplifications made in our model, such as approximating the real DFE system by a series of cylinders.

The density of HF(v = 1) has a linear increase as a function of H_2 FR with a sharp maximum at H_2 FR = 20 sccm, followed by a rapid decrease to a low value which weakly depends on H_2 FR [Fig. 9(c)]. The increase in HF(v = 1) production is dominantly due to reactions (9b) and (9c). The sharp decrease of [HF(v = 1)] at H_2 FR \geq 20 sccm is explained by the combined effect of the fast decrease of [F] and the fast increase of [H_2], leading to enhancement of the collisional quenching at H_2 FR \geq 20 sccm.

Note that HF(v=1) is the only species that has a sharp maximum as a function of H_2 FR and which correlates with the behavior of Si_3N_4/SiO_2 selectivity as a function of H_2 FR shown in Fig. 3. This correlation indicates that HF(v=1) may have an important role in selective Si_3N_4/SiO_2 etching. At the same time, all other species that are potentially important for Si_3N_4 and SiO_2 etching, as presented in Fig. 9, do not show a behavior that can be correlated with selectivity.

The species densities shown in Fig. 9 and their fluxes onto the wafer were used as input to the analytical model for Si_3N_4 and SiO_2 etching. This model is based on the results of quantum chemistry simulations of elementary etching reactions. The results of the model imply an important role for HF molecules in vibrationally exited states in accelerating some etching reactions. Calculations with the analytical model enable us to reproduce the main features of the etching data, in particular, the sharp maximum of Si_3N_4/SiO_2 selectivity versus H_2 FR. The analytical model and predictions of Si_3N_4 and SiO_2 etch rates and Si_3N_4/SiO_2 selectivity are presented in Paper II.⁸

IV. CONCLUDING REMARKS

Measurements of Si₃N₄ and SiO₂ etch rates have been carried out using an NF₃/N₂/O₂/H₂ remote plasma. These measurements show that for some process conditions, it is possible to achieve Si₃N₄/SiO₂ etch selectivity up to 380. The selectivity has a strong maximum as a function of the H₂ flow rate. F-atom and H₂ densities at the wafer level were measured for similar process conditions and are strongly correlated to the H₂ flow rate. The F-atom density has a sharp decrease and H₂ density has a sharp increase in a narrow range of H₂ flow rate. These trends suggest an important role of H₂ in the reaction mechanism. A reaction mechanism for $\rm NF_3/N_2/O_2/H_2$ plasmas and afterglows was developed, and global model simulations of the experimental conditions were conducted. Results from the simulations were compared with experimentally measured F-atom and H₂ densities at the wafer level, and agree well. The experimental data and results of simulations suggest that HF molecules in vibrationally excited states play an important role in selectively etching Si₃N₄ and SiO₂ with NF₃/N₂/O₂/H₂ remote plasmas. These observations have been used for developing a new mechanism of selective Si₃N₄/SiO₂ etching.

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APPENDIX: REACTION MECHANISM FOR NF₃/O₂/H₂ PLASMAS

This appendix contains the additional reactions required for adding H_2 to NF_3/O_2 mixtures. The reaction mechanism for NF_3/O_2 mixtures is discussed in 27.

Species in full reaction mechanism^a

NF ₃	NF ₂	NF	NF_3^+	NF_2^+	NF^+	N ₂
$N_2(v)$	$N_2(A^{3}\sum_{u}^{+})$	$N_2(B^3\Pi_g, higher)$)	Ν	$N(^{2}D)$	N_2^+
N^+	F ₂	$F_2(1^1 \sum_{u=1}^{+})$	F	$F(^{3}S)$	F_2^+	F^+
F^{-}	O ₂	$O_2(v)$	$O_2(a^{-1}\Delta_g)$	$O_2(b^{-1}\sum_{g}^{+})$	О	$O(^{1}D)$
$O(^{1}S)$	O ₃	O_2^+	O^+	O_2^- -0	O ⁻	O_3^-
NO	N ₂ O	NO_2	NO^+	N_2O^+	FO	FNO
H ₂	$H_2(v = 1)$	$H_2(v=2)$	$H_2(v \ge 3)$	$H_2(B^{-1}\sum_{u}^{+}, higher$)	Н
H(n = 2)	H(n=3)	H_2^+	H^+	H^{-}	NH_3	$NH_3(v)$
NH ₂	NH	$\rm NH_3^+$	NH_2^+	NH^+	NH_2^-	HF
HF(v=1)	$HF(v \ge 2)$	HF^+	OH	H_2O	HO_2	H_2O_2
OH ⁺	H_2O^+	OH-	e			

^aFor simplicity in the reaction list, the following notation is used for excited states:

 $N_{2}^{*} \leftrightarrow N_{2}(A^{3}\Sigma_{u}^{u}), N^{*} \leftrightarrow N(^{2}D), F_{2}^{*} \leftrightarrow F_{2}(1^{1}\Sigma_{u}^{u}), F^{*} \leftrightarrow F(^{3}S), O_{2}^{*} \leftrightarrow O_{2}(a^{1}\Delta_{g}), O^{*} \leftrightarrow O(^{1}D), H_{2}^{*} \leftrightarrow H_{2}(B^{1}\Sigma_{u}^{u}), higher), H^{*} \leftrightarrow H(n = 2), H^{**} \leftrightarrow H(n = 3).$



Reactions^a

Process	Rate coefficient ^b	Reference	ΔH^{b} (eV)
Electron impact H ₂ /H			
$e + H_2 \rightarrow H_2 + e$	с	38	d
$e + H_2 \rightarrow H_2(v = 1) + e$	С	38	
$e + H_2 \rightarrow H_2(v = 2) + e$	С	38	
$e + H_2 \rightarrow H_2(v \ge 3) + e$	c	38	
$e + H_2 \rightarrow H + H^-$	с	38	
$e + H_2 \rightarrow H_2^* + e$	С	38	
$e + H_2 \rightarrow H_2^+ + e + e$	с	38	
$e + H_2 \rightarrow H + H + e$	c	38	-7.4
$e + H_2 \rightarrow H + H + e$	c	38	-8.4
$e + H_2 \rightarrow H + H + e$	c	38	-7.2
$e + H_2 \rightarrow H + H^* + e$	c	38	
$e + H_2 \rightarrow H + H^{**} + e$	с	38	
$e + H_2 \rightarrow H + H^+ + e + e$	С	38	
$e + H_2(v=1) \rightarrow H_2(v=1) + e$	С	38	d
$e + H_2(v = 1) \rightarrow H_2(v = 2) + e$	с	38	
$e + H_2(v = 1) \rightarrow H_2(v \ge 3) + e$	с	38	
$e + H_2(v = 1) \rightarrow H_2 + e$	с	38	
$e + H_2(v = 1) \rightarrow H + H^-$	С	38	
$e + H_2(v = 1) \rightarrow H_2^* + e$	с	38	
$e + H_2(v = 1) \rightarrow H_2^+ + e + e$	с	38	
$e + H_2(v = 1) \rightarrow H + H + e$	С	38	-7.4
$e + H_2(v = 1) \rightarrow H + H + e$	с	38	-8.4
$e + H_2(v = 1) \rightarrow H + H + e$	с	38	-7.2
$e + H_2(v = 1) \rightarrow H + H^* + e$	с	38	
$e + H_2(v = 1) \rightarrow H + H^{**} + e$	с	38	
$e + H_2(v = 1) \rightarrow H + H^+ + e + e$	с	38	
$e + H_2(v = 2) \rightarrow H_2(v = 2) + e$	с	38	d
$e + H_2(v = 2) \rightarrow H_2(v \ge 3) + e$	с	38	
$e + H_2(v = 2) \rightarrow H_2(v = 0) + e$	с	38	
$e + H_2(v = 2) \rightarrow H_2 + e$	с	38	
$e + H_2(v = 2) \rightarrow H_2 + e^-$	с	38	
$e + H_2(v = 2) \rightarrow H_2^* + e$	с	38	
$e + H_2(v = 2) \rightarrow H_2^+ + e + e$	с	38	
$e + H_2(v - 2) \rightarrow H_2 + e + e$	с	38	_74
$e + H_2(v - 2) \rightarrow H + H + e$	с	38	-8.4
$e + H_2(v - 2) \rightarrow H + H + e$	с	38	-7 2
$e + H_2(v - 2) \rightarrow H + H^* + e$	с	38	,.2
$e + H_2(v - 2) \rightarrow H + H^{**} + e$	с	38	
$e + H_2(v - 2) \rightarrow H + H^+ + e + e$	с	38	
$e + H_2(v - 2) \rightarrow H_1(v > 3) + e$	с	38	d
$C + \Pi_2(V \ge 3) \rightarrow \Pi_2(V \ge 3) + C$ $e + H_2(V \ge 3) \rightarrow H_2(V = 2) + e$	с	38	
$C + H_2(v \ge 3) \rightarrow H_2(v = 2) + C$ $e + H_2(v \ge 3) \rightarrow H_2(v = 1) + e$	с	38	
$e + H_2(v \ge 3) \rightarrow H_1 + e$	с	38	
$e + H_2(v \ge 3) \rightarrow H + H^-$	с	38	
$C + H_2(V \ge 3) \rightarrow H + H_2$	с	30	
$c + 11_2(v \ge 3) \rightarrow 11_2 + c$ $e + H_1(v \ge 3) \rightarrow H_1^+ + e^{\pm e}$	с	20 38	
$c + 11_2(v \ge 3) \rightarrow 11_2 + c + c$ $a \pm H_1(v \ge 3) \rightarrow H \pm H \pm a$	с	20	7 /
$c + 11_2(v \ge 3) \rightarrow 11 + 11 + c$ $a \pm H_1(v \ge 3) \rightarrow H \pm H \pm a$	с	20 20	-/.4 Q /
$C + 11_2(V \ge J) \rightarrow 11 + 11 + C$	с	20 20	-0.4
$C + 11_2(V \le J) \rightarrow 11 + 11 + C$	с	20 20	-7.2
$e + n_2(v \ge 3) \rightarrow n + n^2 + e$		38	



Process	Rate coefficient ^b	Reference	ΔH^{b} (eV)
$e + H_2(v \ge 3) \rightarrow H + H^{**} + e$	c	38	
$e + H_2(v \ge 3) \rightarrow H + H^+ + e + e$	с	38	
$e + H_2^+ \rightarrow H + H^+ + e$	с	39	-6.8
$e + H_2^{+} \rightarrow H + H$	с	39	-10.8
$e + H_2^{+} \rightarrow H^+ + H^-$	с	40	
$e + H \rightarrow H + e$	c	41	
$e + H \rightarrow H(n = 2) + e$	с	41	
$e + H \rightarrow H(n = 3) + e$	c	41	
$e + H \rightarrow H^+ + e + e$	c	41	
$e + H^+ \rightarrow H$	$4.5 \times 10^{-13} \text{ T}_{-1}^{-1/2}$	est. 42	
$e + e + H^+ \rightarrow H^* + e$	$5.12 \times 10^{-27} T_e^{-4.5}$	est. 42	
Electron impact HF			
$e + HF \rightarrow HF + e$	с, е	43	
$e + HF \rightarrow HF(v = 1) + e$	с	44	
$e + HF \rightarrow HF(v > 2) + e$	c	44	
$e + HF \rightarrow F^- + H$	c	45	
$e + HF \rightarrow H + F + e$	c, e	43	-4.8
$e + HF \rightarrow HF^+ + e + e$	c, e	43	110
$e + HF(y = 1) \rightarrow HF(y = 1) + e$	с, е	43	
$e + HF(y - 1) \rightarrow HF(y > 2) + e$	с	44	
$e + HE(y = 1) \rightarrow HE + e$	с, е	11	
$e + HE(y = 1) \rightarrow F^- + H$	с	45	
$e + HE(v - 1) \rightarrow F + H + e$	с, е	43	_4.8
$C + HF(v = 1) \rightarrow F + H + C$	с, е	43	-4.0
$e + \Pi F(v > 1) \rightarrow \Pi F + e + e$	с, е	43	
$e + HF(v \ge 2) \rightarrow HF(v \ge 2) + e$	c, f	45	
$e + HF(v \ge 2) \rightarrow HF(v = 1) + e$	c, f		
$e + HF(v \ge 2) \rightarrow HF + e$	с	45	
$e + HF(v \ge 2) \rightarrow F + H$	c, e	45	1.0
$e + HF(v \ge 2) \rightarrow F + H + e$	c, e	43	-4.8
$e + HF(v \ge 2) \rightarrow HF + e + e$	$1 - 10^{-7} = \frac{1}{2}$	45	10.1
$e + HF \rightarrow H + F$	1×10 1_e	est. 46	-10.1
Electron impact NH_x	с	47	
$e + NH_3 \rightarrow NH_3 + e$	ç	47	
$e + NH_3 \rightarrow NH_3(v) + e$	e e e e e e e e e e e e e e e e e e e	47	0.5
$e + NH_3 \rightarrow H + NH_2$	c.	47	-0.5
$e + NH_3 \rightarrow NH_2 + H + e$	-	47	-0.8
$e + NH_3 \rightarrow NH + H + H + e$	C .	47	
$e + NH_3 \rightarrow NH_3 + e + e$	-	47	0.1
$e + NH_3 \rightarrow NH_2 + H + e + e$	c o	47	-0.1
$e + NH_3(v) \rightarrow NH_3(v) + e$	s s		
$e + NH_3(v) \rightarrow NH_3 + e$	c, r		
$e + NH_3(v) \rightarrow H^- + NH_2$	c, g		-0.5
$e + NH_3(v) \rightarrow NH_2 + H + e$	~ 6 C 7		-0.8
$e + NH_3(v) \rightarrow NH + H + H + e$	u, g		
$e + NH_3(v) \rightarrow NH_3^+ + e + e$	с, <u>в</u>		
$e + NH_3(v) \rightarrow NH_2^+ + H + e + e$	c, g		-0.1
$e + NH_2 \rightarrow NH_2 + e$	c, g		
$e + NH_2 \rightarrow H^- + NH$	c, g		-1.1
$e + NH_2 \rightarrow NH + H + e$	c, g		-1.4
$e + NH_2 \rightarrow N + H + H + e$	c, g		-1.4



Process	Rate coefficient ^b	Reference	ΔH^{b} (eV)
$e + NH_2 \rightarrow NH_2^+ + e + e$	с	48	
$e + NH_2 \rightarrow NH^+ + H + e + e$	c	48	
$e + NH \rightarrow NH + e$	с, g		
$e + NH \rightarrow N + H + e$	с, g		-2.3
$e + NH \rightarrow NH^+ + e + e$	с	48	
$e + NH \rightarrow N^{+} + H + e + e$	с	48	
$e + NH_3^+ \rightarrow NH_2 + H$	$1 \times 10^{-7} T_e^{-1/2}$	est. 46	-2.9
$e + NH_2^+ \rightarrow NH + H$	$1 \times 10^{-7} T_e^{-1/2}$	est. 46	-1.4
$e + NH^{+} \rightarrow N + H$	$1 \times 10^{-7} T_e^{-1/2}$	est. 46	-10.2
<i>Electron impact</i> H_xO_y			
$e + OH \rightarrow OH + e$	c, h	49	
$e + OH \rightarrow OH^+ + e + e$	с	50	
$e + OH^+ \rightarrow O(^1S) + H$	$1 \times 10^{-7} T_e^{-1/2}$	est. 46	-4.8
$e + H_2O \rightarrow H_2O + e$	c	51	
$e + H_2O \rightarrow H^- + OH$	с	51	-1
$e + H_2O \rightarrow O^- + H_2$	с	51	-0.9
$e + H_2O \rightarrow OH^- + H$	с	51	-0.9
$e + H_2O \rightarrow OH + H + e$	с	51	-2.4
$e + H_2O \rightarrow O + H + H + e$	с	51	-3.8
$e + H_2O \rightarrow H_2O^+ + e + e$	c	51	
$e + H_2O \rightarrow OH^+ + H + e + e$	c	51	
$e + H_2O \rightarrow O^+ + H + H + e + e$	с	51	-1.7
$e + H_2O \rightarrow H_2^+ + O + e + e$	c	51	-9.4
$e + H_2O \rightarrow H^+ + OH + e + e$	c	51	-1.1
$e + H_2O^+ \rightarrow OH + H$	$6.6 \times 10^{-6} \text{ T}_{e}^{-1/2}$	52	-8.3
$e + H_2O^+ \rightarrow O + H + H$	$2.88 \times 10^{-6} T_{e}^{-1/2}$	52	-3.8
$e + H_2O^+ \rightarrow O + H_2$	$2.52 \times 10^{-6} T_e^{-1/2}$	52	-8.4
Radiative transitions			
$H_2^* \rightarrow H_2$	$2.5 \times 10^7 \text{ s}^{-1}$	53	
$HF(v=1) \rightarrow HF$	$1.89 \times 10^2 \text{ s}^{-1}$	54	
$HF(v \ge 2) \rightarrow HF(v = 1)$	$3.88 \times 10^2 \text{ s}^{-1}$	54	
$HF(v \ge 2) \rightarrow HF$	$2.40 \times 10^{1} \text{ s}^{-1}$	54	
Collisional quenching			
$HF(v=1) + M \rightarrow HF + M$	$3.8 \times 10^{-15} T_n^{1/2}$	55	-0.5
$HF(v \ge 2) + M \rightarrow HF(v = 1) + M$	$3.8 \times 10^{-15} T_n^{1/2}$	est. 55	-0.5
$NH_3(v) + M \rightarrow NH_3 + M$	$3 \times 10^{-13} T_n^{1/2}$	est. 56	-0.1
$H_2(v=1) + M \rightarrow H_2 + M$	$7.45 \times 10^{-17} T_n^{4.3}$	57	-0.5
$H_2(v=2) + M \rightarrow H_2(v=1) + M$	$1.49 \times 10^{-16} T_{\rm p}^{4.3}$	57	-0.5
$H_2(v \ge 3) + M \rightarrow H_2(v = 2) + M$	$2.23 \times 10^{-16} T_n^{4.3}$	57	-0.5
$H_2^* + M \rightarrow H_2 + M$	2.1×10^{-9}	58	-13.7
$H^* + M \rightarrow H + M$	1×10^{-8}	59	-10.2
$\mathrm{H}^{\star\star} + \mathrm{M} \to \mathrm{H} + \mathrm{M}$	1×10^{-8}	59	-12
Positive ion-neutral collisions			
$F^+ + HF \rightarrow HF^+ + F$	1×10^{-11}	est. 28 ^{, i}	-1.4
$F^+ + HF(v = 1) \rightarrow HF^+ + F$	1×10^{-11}	est.	-1.9
$F^+ + HF(v \ge 2) \rightarrow HF^+ + F$	1×10^{-11}	est.	-2.4
$F^+ + H_2 \rightarrow H_2^+ + F$	$6.24 imes 10^{-10}$	60	-2
$F^+ + H_2(v=1) \rightarrow H_2^+ + F$	$6.24 imes 10^{-10}$	est. 60	-2.5
$F^+ + H_2(v=2) \rightarrow H_2^+ + F$	$6.24 imes 10^{-10}$	est. 60	-3



Process	Rate coefficient ^b	Reference	ΔH^{b} (eV)
$F^+ + H_2(v \ge 3) \rightarrow H_2^+ + F$	6.24×10^{-10}	est. 60	-3.5
$F^+ + H \rightarrow H^+ + F$	1×10^{-11}	est.	-3.8
$F^+ + H_2O \rightarrow H_2O^+ + F$	1×10^{-11}	est.	-3.9
$F^+ + OH \rightarrow OH^+ + F$	1×10^{-11}	est.	-3.9
$F^+ + NH \rightarrow NH^+ + F$	1×10^{-11}	est.	-3.9
$F^+ + NH_2 \rightarrow NH_2^+ + F$	1×10^{-11}	est.	-6.3
$F^+ + NH_3 \rightarrow NH_3^+ + F$	2.46×10^{-10}	60	-7.3
$F^+ + NH_3(v) \rightarrow NH_3^+ + F$	2.46×10^{-10}	est. 60	-7.4
$F^+ + H_2 \rightarrow H^+ + HF$	3.12×10^{-11}	60	-5.1
$F^+ + H_2(v=1) \rightarrow H^+ + HF$	3.12×10^{-11}	60	-5.6
$F^+ + H_2(v=2) \rightarrow H^+ + HF$	3.12×10^{-11}	60	-6.1
$F^+ + H_2(v \ge 3) \rightarrow H^+ + HF$	3.12×10^{-11}	60	-6.6
$F^+ + NH_3 \rightarrow NH^+ + HF + H$	1.03×10^{-10}	60	-0.9
$F^+ + NH_3 \rightarrow NH_2^+ + HF$	1.62×10^{-9}	60	-7.5
$F^+ + NH_3(v) \rightarrow NH^+ + HF + H$	1.03×10^{-10}	est. 60	-1
$F^+ + NH_3(v) \rightarrow NH_2^+ + HF$	1.62×10^{-9}	est. 60	-7.6
$HF^+ + HF \rightarrow HF^+ + HF$	1×10^{-9}	est.	
$HF^+ + HF(v = 1) \rightarrow HF^+ + HF$	1×10^{-9}	est.	-0.5
$HF^+ + HF(v \ge 2) \rightarrow HF^+ + HF$	1×10^{-9}	est.	-1
$\mathrm{HF}^{+} + \mathrm{F}_{2} \rightarrow \mathrm{F}_{2}^{+} + \mathrm{HF}$	1×10^{-11}	est.	-0.3
$HF^+ + N_2 \rightarrow N_2^+ + HF$	1×10^{-11}	est.	-0.4
$HF^+ + N_2(v) \rightarrow N_2^+ + HF$	1×10^{-11}	est.	-0.7
$\mathrm{HF}^+ + \mathrm{H}_2 \rightarrow \mathrm{H}_2^+ + \mathrm{HF}$	1×10^{-11}	est.	-0.6
$\mathrm{HF}^{+} + \mathrm{H}_{2}(\mathrm{v} = 1) \rightarrow \mathrm{H}_{2}^{+} + \mathrm{HF}$	1×10^{-11}	est.	-1.1
$\mathrm{HF}^{+} + \mathrm{H}_{2}(\mathrm{v} = 2) \rightarrow \mathrm{H}_{2}^{+} + \mathrm{HF}$	1×10^{-11}	est.	-1.6
$\mathrm{HF}^{+} + \mathrm{H}_{2}(\mathrm{v} \geq 3) \rightarrow \mathrm{H}_{2}^{+} + \mathrm{HF}$	1×10^{-11}	est.	-2.1
$HF^+ + N \rightarrow N^+ + HF$	1×10^{-11}	est.	-1.5
$HF^+ + O \rightarrow O^+ + HF$	1×10^{-11}	est.	-2.4
$HF^+ + H \rightarrow H^+ + HF$	1×10^{-11}	est.	-2.4
$\mathrm{HF^{+}} + \mathrm{NF_{3}} \rightarrow \mathrm{NF_{3}^{+}} + \mathrm{HF}$	1×10^{-11}	est.	-2.5
$HF^+ + H_2O \rightarrow H_2O^+ + HF$	1×10^{-11}	est.	-2.5
$HF^+ + OH \rightarrow OH^+ + HF$	1×10^{-11}	est.	-2.5
$HF^+ + NH \rightarrow NH^+ + HF$	1×10^{-11}	est.	-2.5
$HF^+ + N_2O \rightarrow N_2O^+ + HF$	1×10^{-11}	est.	-3.1
$HF^+ + NF \rightarrow NF^+ + HF$	1×10^{-11}	est.	-3.7
$\mathrm{HF^{+}} + \mathrm{O}_{2} \rightarrow \mathrm{O}_{2}^{+} + \mathrm{HF}$	1×10^{-11}	est.	-3.9
$\mathrm{HF}^{+} + \mathrm{O}_{2}(\mathrm{v}) \rightarrow \mathrm{O}_{2}^{+} + \mathrm{HF}$	1×10^{-11}	est.	-4.1
$\mathrm{HF}^{+} + \mathrm{NF}_{2} \rightarrow \mathrm{NF}_{2}^{+} + \mathrm{HF}$	1×10^{-11}	est.	-4.4
$\mathrm{HF}^{+} + \mathrm{NH}_{2} \rightarrow \mathrm{NH}_{2}^{+} + \mathrm{HF}$	1×10^{-11}	est.	-4.9
$\mathrm{HF}^{+} + \mathrm{NH}_{3} \rightarrow \mathrm{NH}_{3}^{+} + \mathrm{HF}$	1×10^{-11}	est.	-5.9
$HF^+ + NH_3(v) \rightarrow NH_3^+ + HF$	1×10^{-11}	est.	-6
$HF^+ + NO \rightarrow NO^+ + HF$	1×10^{-11}	est.	-6.7
$F_2^+ + HF(v=1) \rightarrow HF^+ + F_2$	1×10^{-11}	est.	-0.2
$F_2^+ + HF(v \ge 2) \rightarrow HF^+ + F_2$	1×10^{-11}	est.	-0.7
$F_2^+ + H_2 \rightarrow H_2^+ + F_2$	1×10^{-11}	est.	-0.3
$F_2^+ + H_2(v = 1) \rightarrow H_2^+ + F_2$	1×10^{-11}	est.	-0.8
$F_2^+ + H_2(v=2) \rightarrow H_2^+ + F_2$	1×10^{-11}	est.	-1.3
$F_2^+ + H_2(v \ge 3) \rightarrow H_2^+ + F_2$	1×10^{-11}	est.	-1.8
$F_2^+ + H \rightarrow H^+ + F_2$	1×10^{-11}	est.	-2.1
$F_2^+ + H_2O \rightarrow H_2O^+ + F_2$	1×10^{-11}	est.	-2.2
$F_2^+ + OH \rightarrow OH^+ + F_2$	1×10^{-11}	est.	-2.2



$ \begin{split} & \mathbf{f} + \mathbf{N} \mathbf{I} - \mathbf{N} \mathbf{I}^{-1} + \mathbf{F}_{2} & 1 \times \mathbf{I} 0^{-11} & \text{est} & -22 \\ & \mathbf{f} + \mathbf{N} \mathbf{I}_{2} + \mathbf{N} \mathbf{I}_{2} + \mathbf{N} \mathbf{I}_{3} + \mathbf{F}_{1} & 1 \times \mathbf{I} 0^{-11} & \text{est} & -56 \\ & \mathbf{F}_{1} + \mathbf{N} \mathbf{I}_{3} + \mathbf{N}_{1} + \mathbf{F}_{2} & 1 \times \mathbf{I} 0^{-11} & \text{est} & -56 \\ & \mathbf{F}_{1} + \mathbf{N} \mathbf{I}_{3} + \mathbf{N}_{1} + \mathbf{F}_{2} & 1 \times \mathbf{I} 0^{-11} & \text{est} & -01 \\ & \mathbf{N} + \mathbf{H} (\mathbf{F}_{1} + \mathbf{N}_{2} + \mathbf{N}_{2} + \mathbf{N}_{2} + \mathbf{N}_{2} + \mathbf{N}_{2} + \mathbf{N}_{2} + \mathbf{N}_{2} + \mathbf{N}_{2} + \mathbf{N}_{2} + \mathbf{N}_{2} + \mathbf{N}_{2} + \mathbf{N}_{2} + \mathbf{N}_{2} + \mathbf{N}_{2} + \mathbf{N}_{2} + \mathbf{N}_{2} + \mathbf{N}_{2} + \mathbf{N}_{2} + \mathbf{N}_{2}$	Process	Rate coefficient ^b	Reference	ΔH^{b} (eV)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$F_2^+ + NH \rightarrow NH^+ + F_2$	1×10^{-11}	est.	-2.2
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\tilde{F_2^+} + NH_2 \rightarrow NH_2^+ + \tilde{F_2}$	1×10^{-11}	est.	-4.6
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$F_2^+ + NH_3 \rightarrow NH_3^+ + F_2$	1×10^{-11}	est.	-5.6
$\begin{split} \mathbf{N}_{1}^{*} + \mathbf{H}_{1}^{*}(\mathbf{v}=1) \to \mathbf{H}_{1}^{*} + \mathbf{N}_{2} & 1 \times 10^{-11} & \mathbf{cst} & -0.6 \\ \mathbf{N}_{1}^{*} + \mathbf{H}_{1} \to \mathbf{H}_{2}^{*} + \mathbf{N}_{2} & 17 \times 10^{-11} & \mathbf{cst} & 61 & -0.2 \\ \mathbf{N}_{1}^{*} + \mathbf{H}_{1} \to \mathbf{H}_{2}^{*} + \mathbf{N}_{2} & 17 \times 10^{-11} & \mathbf{cst} & 61 & -0.2 \\ \mathbf{N}_{1}^{*} + \mathbf{H}_{1} (\mathbf{v}=1) \to \mathbf{H}_{2}^{*} + \mathbf{N}_{2} & 17 \times 10^{-11} & \mathbf{cst} & 61 & -0.2 \\ \mathbf{N}_{1}^{*} + \mathbf{H}_{1} (\mathbf{v}=1) \to \mathbf{H}_{2}^{*} + \mathbf{N}_{2} & 17 \times 10^{-11} & \mathbf{cst} & 61 & -1.2 \\ \mathbf{N}_{1}^{*} + \mathbf{H}_{1} (\mathbf{v}=1) \to \mathbf{H}_{2}^{*} + \mathbf{N}_{2} & 17 \times 10^{-11} & \mathbf{cst} & 61 & -1.2 \\ \mathbf{N}_{1}^{*} + \mathbf{H}_{1} (\mathbf{v}=1) \to \mathbf{H}_{2}^{*} + \mathbf{N}_{2} & 17 \times 10^{-11} & \mathbf{cst} & -2 \\ \mathbf{N}_{1}^{*} + \mathbf{H}_{2} \to \mathbf{H}_{2}^{*} + \mathbf{N}_{2} & 17 \times 10^{-11} & \mathbf{cst} & -2 \\ \mathbf{N}_{1}^{*} + \mathbf{H}_{2} \to \mathbf{H}_{1}^{*} + \mathbf{N}_{2} & 17 \times 10^{-11} & \mathbf{cst} & -2 \\ \mathbf{N}_{1}^{*} + \mathbf{H}_{2} \to \mathbf{H}_{1}^{*} + \mathbf{N}_{2} & 17 \times 10^{-11} & \mathbf{cst} & -2 \\ \mathbf{N}_{1}^{*} + \mathbf{N}_{1} \to \mathbf{N}_{1}^{*} + \mathbf{N}_{2} & 17 \times 10^{-11} & \mathbf{cst} & -2 \\ \mathbf{N}_{1}^{*} + \mathbf{N}_{1} \to \mathbf{N}_{1}^{*} + \mathbf{N}_{2} & 17 \times 10^{-11} & \mathbf{cst} & -2 \\ \mathbf{N}_{1}^{*} + \mathbf{N}_{1} \to \mathbf{N}_{1}^{*} + \mathbf{N}_{2} & 17 \times 10^{-11} & \mathbf{cst} & -2 \\ \mathbf{N}_{1}^{*} + \mathbf{N}_{1} \to \mathbf{N}_{1}^{*} + \mathbf{N}_{2} & 17 \times 10^{-11} & \mathbf{cst} & -2 \\ \mathbf{N}_{1}^{*} + \mathbf{N}_{1} \to \mathbf{N}_{1}^{*} + \mathbf{N}_{2} & 17 \times 10^{-11} & \mathbf{cst} & -2 \\ \mathbf{N}_{1}^{*} + \mathbf{N}_{1} \to \mathbf{N}_{1}^{*} + \mathbf{N}_{2} & 17 \times 10^{-11} & \mathbf{cst} & -2 \\ \mathbf{N}_{1}^{*} + \mathbf{N}_{1} \to \mathbf{N}_{1}^{*} + \mathbf{N}_{2} & 17 \times 10^{-11} & \mathbf{cst} & -2 \\ \mathbf{N}_{1}^{*} + \mathbf{N}_{1} \to \mathbf{N}_{1}^{*} + \mathbf{N}_{2} & 17 \times 10^{-11} & \mathbf{cst} & -1 \\ \mathbf{N}_{1}^{*} + \mathbf{N}_{1} \to \mathbf{N}_{1}^{*} + \mathbf{N}_{2} & 17 \times 10^{-11} & \mathbf{cst} & -1 \\ \mathbf{N}_{1}^{*} + \mathbf{N}_{2} \to \mathbf{N}_{1}^{*} + \mathbf{N}_{2} & 17 \times 10^{-11} & \mathbf{cst} & -1 \\ \mathbf{N}_{1}^{*} + \mathbf{N}_{2} \to \mathbf{N}_{1}^{*} + \mathbf{N}_{2} & \mathbf{N}_{1}^{-11} & \mathbf{cst} & -1 \\ \mathbf{N}_{1}^{*} + \mathbf{N}_{2} \to \mathbf{N}_{1}^{*} + \mathbf{N}_{2} & \mathbf{N}_{1}^{-11} & \mathbf{cst} & -1 \\ \mathbf{N}_{1}^{*} + $	$F_2^+ + NH_3(v) \rightarrow NH_3^+ + F_2$	1×10^{-11}	est.	-5.7
$\begin{split} \mathbf{N}^{+} & \mathbf{H}[\mathbf{V} \geq 2) \rightarrow \mathbf{H}^{+} & \mathbf{N}_{2} & 1 \times 10^{-11} & \mathbf{est} & -0.6 \\ \mathbf{N}^{+} & \mathbf{H}_{2} + \mathbf{H}_{2} (\mathbf{v} = 1) \rightarrow \mathbf{H}^{+}_{2} + \mathbf{N}_{2} & 1.7 \times 10^{-11} & \mathbf{est} \cdot 61 & -0.2 \\ \mathbf{N}^{+} & \mathbf{H}_{4}(\mathbf{v} = 2) \rightarrow \mathbf{H}^{+}_{2} + \mathbf{N}_{2} & 1.7 \times 10^{-11} & \mathbf{est} \cdot 61 & -1.2 \\ \mathbf{N}^{+} & \mathbf{H}_{4}(\mathbf{v} = 2) \rightarrow \mathbf{H}^{+}_{2} + \mathbf{N}_{2} & 1.7 \times 10^{-11} & \mathbf{est} \cdot 61 & -1.2 \\ \mathbf{N}^{+} + \mathbf{H}_{4}(\mathbf{v} = 3) \rightarrow \mathbf{H}^{+}_{4} + \mathbf{N}_{2} & 1.7 \times 10^{-11} & \mathbf{est} \cdot 61 & -1.7 \\ \mathbf{N}^{+} + \mathbf{H}_{4} + \mathbf{H}^{+} + \mathbf{N}_{2} & 1 \times 10^{-11} & \mathbf{est} & -2 \\ \mathbf{N}^{+} + \mathbf{N}_{4} + \mathbf{N}_{4} + \mathbf{N}_{4} + \mathbf{N}_{5} & 1 \times 10^{-11} & \mathbf{est} & -2.1 \\ \mathbf{N}^{+} + \mathbf{N}_{4} + \mathbf{N}_{4} + \mathbf{N}_{5} & 1 \times 10^{-11} & \mathbf{est} & -2.1 \\ \mathbf{N}^{+} + \mathbf{N}_{4} + \mathbf{N}_{4} + \mathbf{N}_{5} & 1 \times 10^{-11} & \mathbf{est} & -2.1 \\ \mathbf{N}^{+} + \mathbf{N}_{4} + \mathbf{N}_{4} + \mathbf{N}_{5} & 1 \times 10^{-11} & \mathbf{est} & -2.1 \\ \mathbf{N}^{+} + \mathbf{N}_{4} + \mathbf{N}_{4} + \mathbf{N}_{5} & 1 \times 10^{-9} & \mathbf{est} & -2.1 \\ \mathbf{N}^{+} + \mathbf{N}_{4} + \mathbf{N}_{4} + \mathbf{N}_{5} & 10^{-9} & \mathbf{est} & -1.5 \\ \mathbf{N}^{+} + \mathbf{N}_{4} + \mathbf{N}_{4} + \mathbf{N}_{5} & 10^{-9} & \mathbf{est} & -1.5 \\ \mathbf{H}^{+} + \mathbf{N}_{4} (\mathbf{v} - 1) \rightarrow \mathbf{H}^{+} + \mathbf{H}_{2} & 1 \times 10^{-9} & \mathbf{est} & -1.5 \\ \mathbf{H}^{+} + \mathbf{N}_{4} (\mathbf{v} - 2) \rightarrow \mathbf{H}^{+} + \mathbf{H}_{2} & 1 \times 10^{-11} & \mathbf{est} & -0.0 \\ \mathbf{H}^{+} + \mathbf{H}_{4} (\mathbf{v} - 2) \rightarrow \mathbf{H}^{+} + \mathbf{H}_{2} & 1 \times 10^{-11} & \mathbf{est} & -1.5 \\ \mathbf{H}^{+} + \mathbf{N}_{4} (\mathbf{v} - 1) \rightarrow \mathbf{H}^{+} + \mathbf{H}_{2} & 1 \times 10^{-11} & \mathbf{est} & -1.5 \\ \mathbf{H}^{+} + \mathbf{N}_{4} (\mathbf{v} - 1) \rightarrow \mathbf{H}^{+} + \mathbf{H}_{2} & 1 \times 10^{-11} & \mathbf{est} & -1.5 \\ \mathbf{H}^{+} + \mathbf{N}_{5} (\mathbf{N}^{+} + \mathbf{H}_{2} & 1 \times 10^{-11} & \mathbf{est} & -1.5 \\ \mathbf{H}^{+} + \mathbf{N}_{5} \rightarrow \mathbf{N}^{+} + \mathbf{H}_{2} & 1 \times 10^{-11} & \mathbf{est} & -1.5 \\ \mathbf{H}^{+} + \mathbf{N}_{5} \rightarrow \mathbf{N}^{+} + \mathbf{H}_{2} & 1 \times 10^{-11} & \mathbf{est} & -1.5 \\ \mathbf{H}^{+} + \mathbf{N}_{5} \rightarrow \mathbf{N}^{+} + \mathbf{H}_{2} & 1 \times 10^{-11} & \mathbf{est} & -1.5 \\ \mathbf{H}^{+} + \mathbf{N}_{5} \rightarrow \mathbf{N}^{+} + \mathbf{H}_{2} & \mathbf{N}^{-1} = \mathbf{N}^{-1} & \mathbf{N}^{-1} & \mathbf{N}^{$	$N_2^+ + HF(v=1) \rightarrow HF^+ + N_2$	1×10^{-11}	est.	-0.1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$N_2^+ + HF(v \ge 2) \rightarrow HF^+ + N_2$	1×10^{-11}	est.	-0.6
$\begin{split} \mathbf{N}_{1}^{k} + \mathbf{H}_{1}^{k}(\mathbf{v} = 1) \rightarrow \mathbf{H}_{1}^{k} + \mathbf{N}_{2} & 1^{7} \times 10^{-11} & \mathrm{ext. } 6\mathbf{i} & -0.7 \\ \mathbf{N}_{1}^{k} + \mathbf{H}_{2}^{k}(\mathbf{v} \geq 3) \rightarrow \mathbf{H}_{1}^{k} + \mathbf{N}_{2} & 1^{7} \times 10^{-11} & \mathrm{ext. } 6\mathbf{i} & -1.2 \\ \mathbf{N}_{1}^{k} + \mathbf{H}_{1}^{k} + \mathbf{N}_{2} & 1^{k} \times 10^{-11} & \mathrm{ext. } 6\mathbf{i} & -1.7 \\ \mathbf{N}_{1}^{k} + \mathbf{H}_{1}^{k} + \mathbf{H}_{2}^{k} + \mathbf{N}_{2} & 1^{k} \times 10^{-11} & \mathrm{ext. } 6\mathbf{i} & -1.7 \\ \mathbf{N}_{1}^{k} + \mathbf{H}_{1}^{k} + \mathbf{N}_{2} & 1^{k} \times 10^{-11} & \mathrm{ext. } -2.1 \\ \mathbf{N}_{1}^{k} + \mathbf{N}_{1} + \mathbf{N}_{1}^{k} + \mathbf{N}_{2} & 1^{k} \times 10^{-11} & \mathrm{ext. } -2.1 \\ \mathbf{N}_{1}^{k} + \mathbf{N}_{1} + \mathbf{N}_{1}^{k} + \mathbf{N}_{2} & 1^{k} \times 10^{-11} & \mathrm{ext. } -2.1 \\ \mathbf{N}_{1}^{k} + \mathbf{N}_{1} + \mathbf{N}_{1}^{k} + \mathbf{N}_{2} & 1^{k} \times 10^{-11} & \mathrm{ext. } -4.5 \\ \mathbf{N}_{1}^{k} + \mathbf{N}_{1} + \mathbf{N}_{1}^{k} + \mathbf{N}_{2} & 1^{k} \times 10^{-2} & 6.5 \\ \mathbf{N}_{1}^{k} + \mathbf{N}_{1}^{k} + \mathbf{N}_{1}^{k} + \mathbf{N}_{2} & 1^{k} \times 10^{-2} & 0^{k} & 0^{k} \\ \mathbf{H}_{1}^{k} + 10^{k} + \mathbf{N}_{2} & 1^{k} \times 10^{-2} & 0^{k} & 0^{k} \\ \mathbf{H}_{1}^{k} + \mathbf{N}_{2} + \mathbf{N}_{1}^{k} + \mathbf{N}_{2} & 1^{k} \times 10^{-2} & 0^{k} & 0^{k} \\ \mathbf{H}_{1}^{k} + \mathbf{N}_{2}^{k} + \mathbf{N}_{2} & 1^{k} \times 10^{-2} & 0^{k} & 0^{k} \\ \mathbf{H}_{1}^{k} + \mathbf{N}_{2}^{k} + \mathbf{N}_{2} & 1^{k} \times 10^{-2} & 0^{k} & 0^{k} \\ \mathbf{H}_{1}^{k} + \mathbf{N}_{2}^{k} + \mathbf{N}_{2} & 1^{k} \times 10^{-2} & 0^{k} & 0^{k} \\ \mathbf{H}_{1}^{k} + \mathbf{N}_{2}^{k} + \mathbf{N}_{2} & \mathbf{N}_{1}^{k} + \mathbf{N}_{2} & 1^{k} \times 10^{-11} & 0^{k} \\ \mathbf{H}_{1}^{k} + \mathbf{N}_{2}^{k} + \mathbf{N}_{2}^{k} + \mathbf{N}_{2} & \mathbf{N}_{1}^{k} & \mathbf{N}_{1}^{k} \\ \mathbf{H}_{1}^{k} + \mathbf{N}_{2}^{k} + \mathbf{N}_{2}^{k} + \mathbf{N}_{2} & \mathbf{N}_{1}^{k} = \mathbf{N}_{2}^{k} \\ \mathbf{H}_{1}^{k} + \mathbf{N}_{1}^{k} + \mathbf{N}_{2}^{k} & \mathbf{N}_{1}^{k} \\ \mathbf{H}_{1}^{k} + \mathbf{N}_{2}^{k} + \mathbf{N}_{2}^{k} & \mathbf{N}_{1}^{k} \\ \mathbf{H}_{1}^{k} + \mathbf{N}_{2}^{k} + \mathbf{N}_{2}^{k} \\ \mathbf{H}_{1}^{k} + \mathbf{N}_{2}^{k} + \mathbf{N}_{2}^{k} & \mathbf{N}_{1}^{k} \\ \mathbf{H}_{1}^{k} + \mathbf{N}_{2}^{k} & \mathbf{N}_{1}^{k} \\ \mathbf{H}_{1}^{k} + \mathbf{N}_{2}^{k} + \mathbf{N}_{2}^{k} \\ \mathbf{H}_{1}^{k}$	$N_2^+ + H_2 \rightarrow H_2^+ + N_2$	1.7×10^{-11}	61	-0.2
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$N_2^+ + H_2(v=1) \rightarrow H_2^+ + N_2$	1.7×10^{-11}	est. 61	-0.7
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$N_2^+ + H_2(v=2) \rightarrow H_2^+ + N_2$	1.7×10^{-11}	est. 61	-1.2
$\begin{split} \mathbf{N}_{2}^{4} & \mathbf{H}_{1}^{4} \rightarrow \mathbf{H}_{1}^{4} + \mathbf{N}_{2}^{4} & \mathbf{N}_{1}^{4} & \mathbf{N}_{2}^{4} & \mathbf{N}_{1}^{4} & \mathbf{N}_{2}^{4} & \mathbf{N}_{1}^{4} & \mathbf{N}_{1}^{4} & \mathbf{N}_{2}^{4} & \mathbf{N}_{1}^{4} & \mathbf{N}_{1}^{4} & \mathbf{N}_{1}^{4} & \mathbf{N}_{2}^{4} & \mathbf{N}_{1}^{4} & \mathbf{N}_{1}^{4} & \mathbf{N}_{2}^{4} & \mathbf{N}_{1}^{4} & \mathbf{N}_{1}^{4} & \mathbf{N}_{2}^{4} & \mathbf{N}_{1}^{4} & \mathbf{N}_{1}^{4} & \mathbf{N}_{1}^{4} & \mathbf{N}_{2}^{4} & \mathbf{N}_{1}^{4} & \mathbf{N}_{2}^{4} & $	$N_2^+ + H_2(v \ge 3) \rightarrow H_2^+ + N_2$	1.7×10^{-11}	est. 61	-1.7
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$N_2^+ + H \rightarrow H^+ + N_2$	1×10^{-11}	est.	-2
$\begin{split} & N_2^2 + 0\dot{H} \to 0\dot{H}^2 + N_2^{-} & 1 \times 10^{-11} & \text{est.} & -2.1 \\ & N_2^2 + NH_2 \to NH_2^2 + N_2^{-} & 1 \times 10^{-11} & \text{est.} & -2.1 \\ & N_2^2 + NH_2 \to NH_2^2 + N_2^{-} & 1 \times 10^{-11} & \text{est.} & -2.1 \\ & N_2^2 + NH_2 \to NH_2^2 + N_2 & 1 \times 10^{-11} & \text{est.} & -2.1 \\ & N_2^2 + NH_2 \to NH_2^2 + N_2 & 1 \times 10^{-11} & \text{est.} & -2.1 \\ & N_2^2 + NH_2 \to NH_2^2 + N_2 & 1.95 \times 10^{-9} & \text{est.} & -1.5 \\ & N_2^2 + NH_2 \to NH_2^2 + N_2 & 1.95 \times 10^{-9} & \text{est.} & -1.5 \\ & H_2^2 + H_2 \to H_2^2 + H_2 & 1 \times 10^{-9} & \text{est.} & -1.5 \\ & H_2^2 + H_2 (v = 1) \to H_2^2 + H_2 & 1 \times 10^{-9} & \text{est.} & -1.5 \\ & H_2^2 + H_2 (v = 2) \to H_2^2 + H_2 & 1 \times 10^{-9} & \text{est.} & -1.5 \\ & H_2^2 + N_2 (v > N_1^2 + H_2 & 1 \times 10^{-11} & \text{est.} & -0.4 \\ & H_2^2 + N \to N^2 + H_2 & 1 \times 10^{-11} & \text{est.} & -0.4 \\ & H_2^2 + N \to N^2 + H_2 & 1 \times 10^{-11} & \text{est.} & -1.8 \\ & H_2^2 + N_2 \to N_2^2 + H_2^2 & 1 \times 10^{-11} & \text{est.} & -1.8 \\ & H_2^2 + N_2 \to N_2^2 + H_2 & 1 \times 10^{-11} & \text{est.} & -1.9 \\ & H_2^2 + N_2 \to N_2^2 + H_2 & 1 \times 10^{-11} & \text{est.} & -1.9 \\ & H_2^2 + N_2 \to N_2^2 + H_2 & 1 \times 10^{-11} & \text{est.} & -1.9 \\ & H_2^2 + N_2 \to N_2^2 + H_2 & 1 \times 10^{-11} & \text{est.} & -1.9 \\ & H_2^2 + N_2 \to N_2^2 + H_2 & 1 \times 10^{-11} & \text{est.} & -2.5 \\ & H_2^2 + N_2 \to N_2^2 + H_2 & 1 \times 10^{-11} & \text{est.} & -3.3 \\ & H_2^2 + N_2 \to N_2^2 + H_2 & 1 \times 10^{-11} & \text{est.} & -3.3 \\ & H_2^2 + N_2 \to N_2^2 + H_2 & 1 \times 10^{-11} & \text{est.} & -3.4 \\ & H_2^2 + N_2 \to N_2^2 + H_2 & 1 \times 10^{-11} & \text{est.} & -3.4 \\ & H_2^2 + N_2 \to N_2^2 + H_2 & 1 \times 10^{-11} & \text{est.} & -3.4 \\ & H_2^2 + N_2 \to N_2^2 + H_2 & 1 \times 10^{-11} & \text{est.} & -3.4 \\ & H_2^2 + N_2 \to N_2^2 + H_2 & 1 \times 10^{-11} & \text{est.} & -3.4 \\ & H_2^2 + N_2 \to N_2^2 + H_2 & 1 \times 10^{-11} & \text{est.} & -0.1 \\ & H_2 + N_2 \to N_2^2 + N_2 & 1 \times 10^{-11} & \text{est.} & -0.1 \\ & H_2 + N_3 \to N_1^2 + H_2 & 1 \times 10^{-11} & \text{est.} & -0.4 \\ & H_2 + N_3 \to N_1^2 + N_1 & 1 \times 10^{-11} & \text{est.} & -0.4 \\ & H_2 + N_3 \to N_1^2 + N_1 & 1 \times 10^{-11} & \text{est.} & -0.4 \\ & H_2 + N_1 \to N_1^2 + N_1 & 1 \times 10^{-11} & \text{est.} & -0.4 \\ & H_2 + N_1 \to N_1^2 + N_1 $	$N_2^+ + H_2O \rightarrow H_2O^+ + N_2$	2.3×10^{-9}	62	-2.1
$\begin{split} N_2^n + 8H \to NH^n + N_2 & 1 \times 10^{-11} & \text{est.} & -2.1 \\ N_2^n + NH_2 \to NH_2^n + N_2 & 1 \times 10^{-11} & \text{est.} & -4.5 \\ N_2^n + NH_3 \to NH_3^n + N_2 & 1.95 \times 10^{-9} & \text{6.3} & -5.5 \\ N_2^n + NH_3 (v) \to NH_1^n + N_2 & 1.95 \times 10^{-9} & \text{est.} & -0.5 \\ H_2^n + H_2 (v = 1) \to H_2^n + H_2 & 1 \times 10^{-9} & \text{est.} & -1.5 \\ H_2^n + H_2 (v = 1) \to H_2^n + H_2 & 1 \times 10^{-9} & \text{est.} & -1.5 \\ H_2^n + H_2 (v = 1) \to H_2^n + H_2 & 1 \times 10^{-9} & \text{est.} & -1.5 \\ H_2^n + H_2 (v = 1) \to H_2^n + H_2 & 1 \times 10^{-9} & \text{est.} & -1.5 \\ H_2^n + N_2 (v) \to N_2^n + H_2 & 1 \times 10^{-11} & \text{est.} & -0.1 \\ H_2^n + H_2 (v = 2) \to H_2^n + H_2 & 1 \times 10^{-11} & \text{est.} & -0.1 \\ H_2^n + N_2 (v) \to N_2^n + H_2 & 1 \times 10^{-11} & \text{est.} & -0.1 \\ H_2^n + N^n + H_2 & 1 \times 10^{-11} & \text{est.} & -1.8 \\ H_2^n + N^n + H_2 & 1 \times 10^{-11} & \text{est.} & -1.9 \\ H_2^n + O \to O^n + H_2 & 1 \times 10^{-11} & \text{est.} & -1.9 \\ H_2^n + O \to O^n + H_2 & 1 \times 10^{-11} & \text{est.} & -1.9 \\ H_2^n + O \to O^n + H_2 & 1 \times 10^{-11} & \text{est.} & -1.9 \\ H_2^n + O \to O^n + H_2 & 1 \times 10^{-11} & \text{est.} & -1.9 \\ H_2^n + N^n + H_2 & 1 \times 10^{-11} & \text{est.} & -1.9 \\ H_2^n + N^n + H_2 & 1 \times 10^{-11} & \text{est.} & -1.9 \\ H_2^n + N^n + N^n + H_2 & 1 \times 10^{-11} & \text{est.} & -3.3 \\ H_2^n + O_Q \to O_Q^n + H_2 & 1 \times 10^{-11} & \text{est.} & -3.3 \\ H_2^n + O_Q \to O_Q^n + H_2 & 1 \times 10^{-11} & \text{est.} & -3.3 \\ H_2^n + O_Q \to O_Q^n + H_2 & 1 \times 10^{-11} & \text{est.} & -3.3 \\ H_2^n + N_Q \to N_Q^n + H_2 & 1 \times 10^{-11} & \text{est.} & -3.3 \\ H_2^n + N_Q \to N_Q^n + H_2 & 1 \times 10^{-11} & \text{est.} & -3.4 \\ H_2^n + N_Q \to N_Q^n + H_2 & 1 \times 10^{-11} & \text{est.} & -3.4 \\ H_2^n + N_Q \to N_Q^n + H_2 & 1 \times 10^{-11} & \text{est.} & -0.1 \\ N^n + H_2 (v = 2) \to H_2^n + N & 1 \times 10^{-11} & \text{est.} & -0.1 \\ N^n + H_2 (v = 2) \to H_2^n + N & 1 \times 10^{-11} & \text{est.} & -0.1 \\ N^n + H_2 (v = 2) \to H_2^n + N & 1 \times 10^{-11} & \text{est.} & -0.1 \\ N^n + H_2 (v = 2) \to H_2^n + N & 1 \times 10^{-11} & \text{est.} & -1.1 \\ N^n + N_H \to NH_2^n + N & 1 \times 10^{-11} & \text{est.} & -1.1 \\ N^n + N_H \to NH_2^n + N & 1 \times 10^{-11} & \text{est.} & -1.1 \\ N^n + N_H \to NH_2^n + N & 1 \times 10^{-11} & \text{est.}$	$N_2^+ + OH \rightarrow OH^+ + N_2$	1×10^{-11}	est.	-2.1
$\begin{split} & \begin{array}{ccccccccccccccccccccccccccccccccccc$	$N_2^+ + NH \rightarrow NH^+ + N_2$	1×10^{-11}	est.	-2.1
$\begin{split} & \begin{array}{ccccccccccccccccccccccccccccccccccc$	$N_2^+ + NH_2 \rightarrow NH_2^+ + N_2$	1×10^{-11}	est.	-4.5
$\begin{split} & N_2^* + N H_3(\mathbf{y}) \to N H_2^* + N_2 & 1.95 \times 10^{-9} & \text{est. } 63 & -5.6 \\ & H_2^* + H_2 \to H_2^* + H_2 & 1 \times 10^{-9} & \text{est.} & -0.5 \\ & H_2^* + H_2(\mathbf{y} \geq 2) \to H_2^* + H_2 & 1 \times 10^{-9} & \text{est.} & -1.5 \\ & H_2^* + H_2(\mathbf{y} \geq 3) \to H_2^* + H_2 & 1 \times 10^{-11} & \text{est.} & -1.5 \\ & H_2^* + H_2(\mathbf{y} \geq 3) \to H_2^* + H_2 & 1 \times 10^{-11} & \text{est.} & -0.4 \\ & H_2^* + N \to N^* + H_2 & 1 \times 10^{-11} & \text{est.} & -0.4 \\ & H_2^* + N \to N^* + H_2 & 1 \times 10^{-11} & \text{est.} & -0.9 \\ & H_2^* + N \to N^* + H_2 & 1 \times 10^{-11} & \text{est.} & -1.8 \\ & H_2^* + N \to N^* + H_2 & 1 \times 10^{-11} & \text{est.} & -1.9 \\ & H_2^* + N \to N^* + H_2 & 1 \times 10^{-11} & \text{est.} & -1.9 \\ & H_2^* + N \to N^* + H_2 & 1 \times 10^{-11} & \text{est.} & -1.9 \\ & H_2^* + N \to N^* + H_2 & 1 \times 10^{-11} & \text{est.} & -1.9 \\ & H_2^* + N \to N^* + H_2 & 1 \times 10^{-11} & \text{est.} & -1.9 \\ & H_2^* + N \to N^* + H_2 & 1 \times 10^{-11} & \text{est.} & -1.9 \\ & H_2^* + N \to N^* + H_2 & 1 \times 10^{-11} & \text{est.} & -1.9 \\ & H_2^* + N \to N^* + H_2 & 1 \times 10^{-11} & \text{est.} & -3.1 \\ & H_2^* + N \to N^* + H_2 & 1 \times 10^{-11} & \text{est.} & -3.5 \\ & H_2^* + N \to N^* + H_2 & 1 \times 10^{-11} & \text{est.} & -3.5 \\ & H_2^* + N \to N^* + H_2 & 1 \times 10^{-11} & \text{est.} & -3.5 \\ & H_2^* + N \to N^* + H_2 & 1 \times 10^{-11} & \text{est.} & -3.5 \\ & H_2^* + N \to N^* + H_2 & 1 \times 10^{-11} & \text{est.} & -3.5 \\ & H_2^* + N \to N^* + H_2 & 1 \times 10^{-11} & \text{est.} & -3.5 \\ & H_2^* + N \to N^* + H_2 & 1 \times 10^{-11} & \text{est.} & -3.5 \\ & H_2^* + N \to N^* + H_2 & 1 \times 10^{-11} & \text{est.} & -3.5 \\ & H_2^* + N \to N^* + H_2 & 1 \times 10^{-11} & \text{est.} & -0.1 \\ & N^* + H_2(\mathbf{v} \geq 0) + H_2^* + N & 1 \times 10^{-11} & \text{est.} & -0.1 \\ & N^* + H_2(\mathbf{v} \geq 0) + H_2^* + N & 1 \times 10^{-11} & \text{est.} & -1.1 \\ & N^* + H_2(\mathbf{v} \geq 0) + H_2^* + N & 1 \times 10^{-11} & \text{est.} & -1.0 \\ & N^* + H_2(\mathbf{v} \geq 0) + H_2^* + N & 1 \times 10^{-11} & \text{est.} & -1.1 \\ & N^* + H_2(\mathbf{v} \geq 0) + H_2^* + N & 1 \times 10^{-11} & \text{est.} & -1.0 \\ & N^* + H_2(\mathbf{v} \geq 0) + H_2^* + N & 1 \times 10^{-11} & \text{est.} & -1.0 \\ & N^* + H_2(\mathbf{v} \geq 0) + H_2^* + N & 1 \times 10^{-11} & \text{est.} & -1.0 \\ & N^* + H_2(\mathbf{v} \geq 0) + H_2^* + N & 1 \times 10^{-11} & \text$	$N_2^+ + NH_3 \rightarrow NH_3^+ + N_2$	1.95×10^{-9}	63	-5.5
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$N_2^+ + NH_3(v) \rightarrow NH_3^+ + N_2$	1.95×10^{-9}	est. 63	-5.6
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$H_2^+ + H_2 \rightarrow H_2^+ + H_2$	1×10^{-9}	est.	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$H_2^+ + H_2(v=1) \rightarrow H_2^+ + H_2$	1×10^{-9}	est.	-0.5
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$H_2^+ + H_2(v=2) \rightarrow H_2^+ + H_2$	1×10^{-9}	est.	-1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$H_2^+ + H_2(v \ge 3) \to H_2^+ + H_2$	1×10^{-9}	est.	-1.5
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$H_2^+ + N_2(v) \rightarrow N_2^+ + H_2$	1×10^{-11}	est.	-0.1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$H_2^+ + HF(v \ge 2) \rightarrow HF^+ + H_2$	1×10^{-11}	est.	-0.4
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$H_2^+ + N \rightarrow N^+ + H_2$	1×10^{-11}	est.	-0.9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$H_2^+ + O \rightarrow O^+ + H_2$	1×10^{-11}	est.	-1.8
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$H_2^+ + H \rightarrow H^+ + H_2^-$	6.4×10^{-10}	64	-1.8
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$H_2^+ + NF_3 \rightarrow NF_3^+ + H_2$	1×10^{-11}	est.	-1.9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$H_2^+ + H_2O \rightarrow H_2O^+ + H_2$	1×10^{-11}	est.	-1.9
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$H_2^+ + OH \rightarrow OH^+ + H_2$	1×10^{-11}	est.	-1.9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$H_2^+ + NH \rightarrow NH^+ + H_2$	1×10^{-11}	est.	-1.9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$H_2^+ + N_2O \rightarrow N_2O^+ + H_2$	1×10^{-11}	est.	-2.5
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$H_2^+ + NF \rightarrow NF^+ + H_2$	1×10^{-11}	est.	-3.1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$H_2^+ + O_2 \rightarrow O_2^+ + H_2$	1×10^{-11}	est.	-3.3
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$H_2^+ + O_2(v) \rightarrow O_2^+ + H_2$	1×10^{-11}	est.	-3.5
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$H_2^+ + NF_2 \rightarrow NF_2^+ + H_2$	1×10^{-11}	est.	-3.8
$\begin{array}{cccccccc} H_2^+ \times H_3 \rightarrow NH_3^+ + H_2 & 5.7 \times 10^{-9} & 65 & -5.3 \\ H_2^+ \times H_3(v) \rightarrow NH_3^+ + H_2 & 5.7 \times 10^{-9} & est. 65 & -5.4 \\ H_2^+ \times NO \rightarrow NO^+ + H_2 & 1 \times 10^{-11} & est. & -6.1 \\ N^+ + H_2(v=2) \rightarrow H_2^+ + N & 1 \times 10^{-11} & est. & -0.1 \\ N^+ + H_2(v\geq 3) \rightarrow H_2^+ + N & 1 \times 10^{-11} & est. & -0.6 \\ N^+ + H \rightarrow H^+ + N & 1 \times 10^{-11} & est. & -0.9 \\ N^+ + H_2O \rightarrow H_2O^+ + N & 1.19 \times 10^{-9} & 62 & -1 \\ N^+ + OH \rightarrow OH^+ + N & 1 \times 10^{-11} & est. & -1 \\ N^+ + NH \rightarrow NH^+ + N & 1 \times 10^{-11} & est. & -1 \\ N^+ + NH_2 \rightarrow NH_2^+ + N & 1 \times 10^{-11} & est. & -1 \\ N^+ + NH_3 \rightarrow NH_3^+ + N & 1.67 \times 10^{-9} & 66 & -4.4 \\ N^+ + NH_3(v) \rightarrow NH_3^+ + N & 1.67 \times 10^{-9} & est. 66 & -4.5 \\ N^+ + H_2(v=1) \rightarrow NH^+ + H & 5 \times 10^{-10} & 67 & 0.2 \\ N^+ + H_2(v=2) \rightarrow NH^+ + H & 5 \times 10^{-10} & 67 & -0.3 \\ N^+ + H_2(v=2) \rightarrow NH^+ + H & 5 \times 10^{-10} & 67 & -0.3 \\ N^+ + H_2(v=2) \rightarrow NH^+ + H & 5 \times 10^{-10} & 67 & -0.8 \\ \end{array}$	$H_2^+ + NH_2 \rightarrow NH_2^+ + H_2$	1×10^{-11}	est.	-4.3
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$H_2^+ + NH_3 \rightarrow NH_3^+ + H_2$	5.7×10^{-9}	65	-5.3
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\mathrm{H}_{2}^{+} + \mathrm{NH}_{3}(\mathrm{v}) \rightarrow \mathrm{NH}_{3}^{+} + \mathrm{H}_{2}$	5.7×10^{-9}	est. 65	-5.4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$H_2^+ + NO \rightarrow NO^+ + H_2$	1×10^{-11}	est.	-6.1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$N^+ + H_2(v=2) \rightarrow H_2^+ + N$	1×10^{-11}	est.	-0.1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$N^+ + H_2(v \ge 3) \rightarrow H_2^+ + N$	1×10^{-11}	est.	-0.6
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$N^+ + H \rightarrow H^+ + N$	1×10^{-11}	est.	-0.9
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$N^+ + H_2O \rightarrow H_2O^+ + N$	1.19×10^{-9}	62	-1
$ \begin{array}{ccccc} N^{+} + NH \rightarrow NH^{+} + N & 1 \times 10^{-11} & \text{est.} & -1 \\ N^{+} + NH_{2} \rightarrow NH_{2}^{+} + N & 1 \times 10^{-11} & \text{est.} & -3.4 \\ N^{+} + NH_{3} \rightarrow NH_{3}^{+} + N & 1.67 \times 10^{-9} & 66 & -4.4 \\ N^{+} + NH_{3}(v) \rightarrow NH_{3}^{+} + N & 1.67 \times 10^{-9} & \text{est.} & 66 & -4.5 \\ N^{+} + H_{2} \rightarrow NH^{+} + H & 5 \times 10^{-10} & 67 & 0.2 \\ N^{+} + H_{2}(v = 1) \rightarrow NH^{+} + H & 5 \times 10^{-10} & 67 & -0.3 \\ N^{+} + H_{2}(v = 2) \rightarrow NH^{+} + H & 5 \times 10^{-10} & 67 & -0.8 \\ \end{array} $	$N^+ + OH \rightarrow OH^+ + N$	1×10^{-11}	est.	-1
$\begin{array}{cccc} N^{+} + NH_{2} \rightarrow NH_{2}^{+} + N & 1 \times 10^{-11} & \text{est.} & -3.4 \\ N^{+} + NH_{3} \rightarrow NH_{3}^{+} + N & 1.67 \times 10^{-9} & 66 & -4.4 \\ N^{+} + NH_{3}(v) \rightarrow NH_{3}^{+} + N & 1.67 \times 10^{-9} & \text{est.} & 66 & -4.5 \\ N^{+} + H_{2} \rightarrow NH^{+} + H & 5 \times 10^{-10} & 67 & 0.2 \\ N^{+} + H_{2}(v = 1) \rightarrow NH^{+} + H & 5 \times 10^{-10} & 67 & -0.3 \\ N^{+} + H_{2}(v = 2) \rightarrow NH^{+} + H & 5 \times 10^{-10} & 67 & -0.8 \end{array}$	$N^+ + NH \rightarrow NH^+ + N$	1×10^{-11}	est.	-1
$\begin{array}{cccc} N^{+} + NH_{3} \rightarrow NH_{3}^{+} + N & 1.67 \times 10^{-9} & 66 & -4.4 \\ N^{+} + NH_{3}(v) \rightarrow NH_{3}^{+} + N & 1.67 \times 10^{-9} & \text{est. } 66 & -4.5 \\ N^{+} + H_{2} \rightarrow NH^{+} + H & 5 \times 10^{-10} & 67 & 0.2 \\ N^{+} + H_{2}(v = 1) \rightarrow NH^{+} + H & 5 \times 10^{-10} & 67 & -0.3 \\ N^{+} + H_{2}(v = 2) \rightarrow NH^{+} + H & 5 \times 10^{-10} & 67 & -0.8 \end{array}$	$N^+ + NH_2 \rightarrow NH_2^+ + N$	1×10^{-11}	est.	-3.4
$\begin{array}{cccc} N^{+} + NH_{3}(v) \rightarrow NH_{3}^{+} + N & 1.67 \times 10^{-9} & est. \ 66 & -4.5 \\ N^{+} + H_{2} \rightarrow NH^{+} + H & 5 \times 10^{-10} & 67 & 0.2 \\ N^{+} + H_{2}(v=1) \rightarrow NH^{+} + H & 5 \times 10^{-10} & 67 & -0.3 \\ N^{+} + H_{2}(v=2) \rightarrow NH^{+} + H & 5 \times 10^{-10} & 67 & -0.8 \end{array}$	$\mathrm{N^{+}+NH_{3}\rightarrow NH_{3}^{+}+N}$	1.67×10^{-9}	66	-4.4
$\begin{array}{cccc} N^{+} + H_{2} \rightarrow NH^{+} + H & 5 \times 10^{-10} & 67 & 0.2 \\ N^{+} + H_{2}(v=1) \rightarrow NH^{+} + H & 5 \times 10^{-10} & 67 & -0.3 \\ N^{+} + H_{2}(v=2) \rightarrow NH^{+} + H & 5 \times 10^{-10} & 67 & -0.8 \end{array}$	$N^+ + NH_3(v) \rightarrow NH_3^+ + N$	1.67×10^{-9}	est. 66	-4.5
$\begin{array}{ccc} N^{+} + H_{2}(v=1) \rightarrow NH^{+} + H & 5 \times 10^{-10} & 67 & -0.3 \\ N^{+} + H_{2}(v=2) \rightarrow NH^{+} + H & 5 \times 10^{-10} & 67 & -0.8 \end{array}$	$N^+ + H_2 \rightarrow NH^+ + H$	5×10^{-10}	67	0.2
$N^{+} + H_{2}(v = 2) \rightarrow NH^{+} + H$ 5×10^{-10} 67 -0.8	$N^+ + H_2(v=1) \rightarrow NH^+ + H$	5×10^{-10}	67	-0.3
	$\mathrm{N^{+}} + \mathrm{H_{2}}(\mathrm{v} = 2) \rightarrow \mathrm{NH^{+}} + \mathrm{H}$	5×10^{-10}	67	-0.8



$\begin{array}{cccc} N^{+} + H_2(v \geq 3) \rightarrow NH^{+} + H & 5 \times 10^{-10} & 67 \\ N^{+} + NH_3 \rightarrow NH_2^{+} + NH & 4.7 \times 10^{-10} & 66 \\ N^{+} + NH_3(v) \rightarrow NH_2^{+} + NH & 4.7 \times 10^{-10} & est. & 66 \\ N^{+} + H_2O \rightarrow NO^{+} + H_2 & 2.1 \times 10^{-10} & 62 \\ O^{+} + H \rightarrow H^{+} + O & 1 \times 10^{-11} & est. \\ O^{+} + H_2O \rightarrow H_2O^{+} + O & 3.2 \times 10^{-9} & est. \\ O^{+} + OH \rightarrow OH^{+} + O & 1 \times 10^{-11} & est. \\ O^{+} + NH \rightarrow NH^{+} + O & 1 \times 10^{-11} & est. \\ \end{array}$	$\begin{array}{r} -1.3 \\ -2 \\ -2.1 \\ -6.7 \\ \hline \\ -0.1 \\ -0.1 \\ -2.5 \\ -3.5 \\ -3.6 \\ \hline \\ -0.1 \\ -0.1 \\ \end{array}$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{r} -2 \\ -2.1 \\ -6.7 \\ \end{array}$
$ \begin{array}{cccc} N^{+} + NH_{3}(v) \rightarrow NH_{2}^{+} + NH & 4.7 \times 10^{-10} & \text{est. } 66 \\ N^{+} + H_{2}O \rightarrow NO^{+} + H_{2} & 2.1 \times 10^{-10} & 62 \\ O^{+} + H \rightarrow H^{+} + O & 1 \times 10^{-11} & \text{est.} \\ O^{+} + H_{2}O \rightarrow H_{2}O^{+} + O & 3.2 \times 10^{-9} & \text{est.} \\ O^{+} + OH \rightarrow OH^{+} + O & 1 \times 10^{-11} & \text{est.} \\ O^{+} + NH \rightarrow NH^{+} + O & 1 \times 10^{-11} & \text{est.} \\ \end{array} $	$\begin{array}{r} -2.1 \\ -6.7 \\ \hline \\ -0.1 \\ -0.1 \\ -2.5 \\ -3.5 \\ -3.6 \\ \hline \\ -0.1 \\ -0.1 \end{array}$
$ \begin{array}{cccc} N^{+} + H_2O \rightarrow NO^{+} + H_2 & 2.1 \times 10^{-10} & 62 \\ O^{+} + H \rightarrow H^{+} + O & 1 \times 10^{-11} & \text{est.} \\ O^{+} + H_2O \rightarrow H_2O^{+} + O & 3.2 \times 10^{-9} & \text{est.} \\ O^{+} + OH \rightarrow OH^{+} + O & 1 \times 10^{-11} & \text{est.} \\ O^{+} + NH \rightarrow NH^{+} + O & 1 \times 10^{-11} & \text{est.} \\ \end{array} $	-6.7 -0.1 -0.1 -2.5 -3.5 -3.6 -0.1 -0.1
$\begin{array}{cccc} O^{+} + H \to H^{+} + O & 1 \times 10^{-11} & \text{est.} \\ O^{+} + H_2 O \to H_2 O^{+} + O & 3.2 \times 10^{-9} & \text{est.} \\ O^{+} + OH \to OH^{+} + O & 1 \times 10^{-11} & \text{est.} \\ O^{+} + NH \to NH^{+} + O & 1 \times 10^{-11} & \text{est.} \end{array}$	$\begin{array}{c} -0.1 \\ -0.1 \\ -2.5 \\ -3.5 \\ -3.6 \end{array}$
$\begin{array}{ccc} O^{+} + H_2 O \to H_2 O^{+} + O & 3.2 \times 10^{-9} & \text{est.} \\ O^{+} + OH \to OH^{+} + O & 1 \times 10^{-11} & \text{est.} \\ O^{+} + NH \to NH^{+} + O & 1 \times 10^{-11} & \text{est.} \end{array}$	$-0.1 \\ -0.1 \\ -0.1 \\ -2.5 \\ -3.5 \\ -3.6 \\ -0.1 \\ -0.1 \\ -0.1 \\$
$\begin{array}{ccc} O^{+} + OH \rightarrow OH^{+} + O & 1 \times 10^{-11} & \text{est.} \\ O^{+} + NH \rightarrow NH^{+} + O & 1 \times 10^{-11} & \text{est.} \end{array}$	$-0.1 \\ -0.1 \\ -2.5 \\ -3.5 \\ -3.6 \\ -0.1 \\ -0.1 \\ -0.1$
$O^+ + NH \rightarrow NH^+ + O$ 1×10^{-11} est.	-0.1 -2.5 -3.5 -3.6 -0.1 -0.1
	-2.5 -3.5 -3.6 -0.1 -0.1
$O^+ + NH_2 \rightarrow NH_2^+ + O$ 1×10^{-11} est.	-3.5 -3.6 -0.1 -0.1
$O^+ + NH_3 \rightarrow NH_3^+ + O$ 1×10^{-11} est.	-3.6 -0.1 -0.1
$O^+ + NH_3(v) \to NH_3^+ + O$ 1×10^{-11} est.	-0.1 -0.1
$H^+ + H \rightarrow H^+ + H$ 1×10^{-9} est.	-0.1 -0.1
$H^+ + O \to O^+ + H$ 3.8×10^{-10} 62	$-0.1 \\ -0.1$
$H^+ + NF_3 \rightarrow NF_3^+ + H$ 1×10^{-11} est.	-0.1
$H^+ + H_2O \to H_2O^+ + H$ 8.2×10^{-9} 62	
$H^+ + OH \rightarrow OH^+ + H$ 1×10^{-11} est.	-0.1
$H^+ + NH \rightarrow NH^+ + H$ 1×10^{-11} est.	-0.1
$H^+ + N_2O \to N_2O^+ + H$ 1×10^{-11} est.	-0.7
$H^+ + NF \rightarrow NF^+ + H$ 1×10^{-11} est.	-1.3
$H^+ + O_2 \rightarrow O_2^+ + H$ 1.17×10^{-9} 62	-1.5
$H^+ + NF_2 \rightarrow NF_2^+ + H$ 1×10^{-11} est.	-2
$H^+ + NH_2 \rightarrow NH_2^+ + H$ 1×10^{-11} est.	-2.5
$H^+ + NH_3 \rightarrow NH_3^+ + H$ 1×10^{-11} est.	-3.5
$H^+ + NH_3(v) \rightarrow NH_3^+ + H$ 1×10^{-11} est.	-3.6
$H^+ + NO \rightarrow NO^+ + H$ 1.9×10^{-9} 62	-4.3
$NF_3^+ + H_2O \rightarrow H_2O^+ + NF_3$ 1×10^{-11} est.	
$NF_2^+ + OH \rightarrow OH^+ + NF_2$ 1×10^{-11} est.	
$NF_2^+ + NH \rightarrow NH^+ + NF_2$ 1×10^{-11} est.	
$NF_{2}^{+} + NH_{2} \rightarrow NH_{2}^{+} + NF_{2}$ 1×10^{-11} est.	-2.4
$NF_3^+ + NH_3^- \rightarrow NH_3^+ + NF_3$ 1×10^{-11} est.	-3.4
$NF_{2}^{+} + NH_{2}(y) \rightarrow NH_{2}^{+} + NF_{2}$ 1×10^{-11} est.	-3.5
$H_2O^+ + H_2O^- + H_2O^- + H_2O^-$ 1×10 ⁻⁹ est.	
$H_2O^+ + NF_2 \rightarrow NF_2^+ + H_2O$ 1×10^{-11} est.	
$H_2O^+ + OH \rightarrow OH^+ + H_2O$ 1×10^{-11} est.	
$H_2O^+ + NH \rightarrow NH^+ + H_2O$ 1×10^{-11} est.	
$H_2O^+ + N_2O \rightarrow N_2O^+ + H_2O$ 1×10^{-11} est.	-0.6
$H_2O^+ + NF \rightarrow NF^+ + H_2O^ 1 \times 10^{-11}$ est.	-1.2
$H_2O^+ + O_2 \rightarrow O_2^+ + H_2O$ 4.3×10^{-10} 62	-1.4
$H_2O^+ + NF_2 \rightarrow NF_2^+ + H_2O$ 1×10^{-11} est.	-1.9
$H_2O^+ + NH_2 \rightarrow NH_2^+ + H_2O$ 1×10^{-11} est.	-2.4
$H_2O^+ + NH_3 \rightarrow NH_3^+ + H_2O$ 1×10^{-11} est.	-3.4
$H_2O^+ + NH_2(y) \rightarrow NH_2^+ + H_2O$ 1×10^{-11} est.	-3.5
$H_2O^+ + NO \rightarrow NO^+ + H_2O$ 4.6×10^{-10} 62	-4.2
$H_2O^+ + N \to NO^+ + H_2$ 1.9×10^{-10} 62	-5.6
$H_2O^+ + O \rightarrow O_2^+ + H_2$ 5.5×10^{-11} 62	-1.5
$OH^+ + OH \rightarrow OH^+ + OH$ 1×10^{-9} est.	
$OH^+ + NF_3 \rightarrow NF_3^+ + OH$ 1×10^{-11} est.	
$OH^+ + H_2O \rightarrow H_2O^+ + OH$ 1×10^{-11} est.	
$OH^+ + NH \rightarrow NH^+ + OH$ 1×10^{-11} est.	
$OH^+ + N_2O \rightarrow N_2O^+ + OH$ 2.13×10^{-10} 62	-0.6
$OH^+ + NF \rightarrow NF^+ + OH$ 1×10^{-11} est.	-1.2



Process	Rate coefficient ^b	Reference	ΔH^{b} (eV)
$OH^+ + O_2 \rightarrow O_2^+ + OH$	1×10^{-11}	est.	-1.4
$OH^+ + NF_2 \rightarrow NF_2^+ + OH$	1×10^{-11}	est.	-1.9
$OH^+ + NH_2 \rightarrow NH_2^+ + OH$	1×10^{-11}	est.	-2.4
$OH^+ + NH_3 \rightarrow NH_3^+ + OH$	1×10^{-11}	est.	-3.4
$OH^+ + NH_3(v) \rightarrow NH_3^+ + OH$	1×10^{-11}	est.	-3.5
$OH^+ + NO \rightarrow NO^+ + OH$	1×10^{-11}	est.	-4.2
$\rm NH^+ + NH \rightarrow NH^+ + NH$	1×10^{-9}	est.	
$NH^+ + NF_3 \rightarrow NF_3^+ + NH$	1×10^{-11}	est.	
$\rm NH^+ + H_2O \rightarrow H_2O^+ + NH$	1×10^{-11}	est.	
$\rm NH^+ + OH \rightarrow OH^+ + NH$	1×10^{-11}	est.	
$\rm NH^+ + N_2O \rightarrow N_2O^+ + NH$	1×10^{-11}	est.	-0.6
$\rm NH^+ + NF \rightarrow NF^+ + NH$	1×10^{-11}	est.	-1.2
$\rm NH^+ + O_2 \rightarrow O_2^+ + NH$	1×10^{-11}	est.	-1.4
$\rm NH^+ + NF_2 \rightarrow NF_2^+ + NH$	1×10^{-11}	est.	-1.9
$\rm NH^+ + \rm NH_2 \rightarrow \rm NH_2^+ + \rm NH$	1×10^{-11}	est.	-2.4
$\rm NH^+ + \rm NH_3 \rightarrow \rm NH_3^+ + \rm NH$	1.8×10^{-9}	68	-3.4
$NH^+ + NH_3(v) \rightarrow NH_3^+ + NH$	1.8×10^{-9}	est. 68	-3.5
$\rm NH^+ + \rm NO \rightarrow \rm NO^+ + \rm NH$	1×10^{-11}	est.	-4.2
$\rm NH^+ + H_2 \rightarrow \rm NH_2^+ + H$	1.05×10^{-9}	68	-2
$N_2O^+ + NH_2 \rightarrow NH_2^+ + N_2O$	1×10^{-11}	est.	-1.8
$N_2O^+ + NH_3 \rightarrow NH_3^+ + N_2O$	1×10^{-11}	est.	-2.8
$N_2O^+ + NH_3(v) \rightarrow NH_3^+ + N_2O$	1×10^{-11}	est.	-2.9
$NF^+ + NH_2 \rightarrow NH_2^+ + NF$	1×10^{-11}	est.	-1.2
$NF^+ + NH_3 \rightarrow NH_3^+ + NF$	1×10^{-11}	est.	-2.2
$NF^+ + NH_3(v) \rightarrow NH_3^+ + NF$	1×10^{-11}	est.	-2.3
$O_2^+ + NH_2 \rightarrow NH_2^+ + O_2$	1×10^{-11}	est.	-1
$O_2^+ + NH_3 \rightarrow NH_3^+ + O_2$	1×10^{-11}	est.	-2
$O_2^+ + NH_3(v) \rightarrow NH_3^+ + O_2$	1×10^{-11}	est.	-2.1
$NF_2^+ + NH_2 \rightarrow NH_2^+ + NF_2$	1×10^{-11}	est.	-0.5
$NF_2^+ + NH_3 \rightarrow NH_3^+ + NF_2$	1×10^{-11}	est.	-1.5
$NF_2^+ + NH_3(v) \rightarrow NH_3^+ + NF_2$	1×10^{-11}	est.	-1.6
$\mathrm{NH}_2^+ + \mathrm{NH}_2 \rightarrow \mathrm{NH}_2^+ + \mathrm{NH}_2$	1×10^{-9}	est.	
$\mathrm{NH}_2^+ + \mathrm{NH}_3 \rightarrow \mathrm{NH}_3^+ + \mathrm{NH}_2$	1.15×10^{-9}	68	-1
$\mathrm{NH}_2^+ + \mathrm{NH}_3(\mathrm{v}) \rightarrow \mathrm{NH}_3^+ + \mathrm{NH}_2$	1.15×10^{-9}	est. 68	-1.1
$\rm NH_2^+ + \rm NO \rightarrow \rm NO^+ + \rm NH_2$	1×10^{-11}	est.	-1.8
$\mathrm{NH}_2^+ + \mathrm{H}_2 \rightarrow \mathrm{NH}_3^+ + \mathrm{H}$	1.95×10^{-10}	68	-1.2
$\mathrm{NH}_3^+ + \mathrm{NH}_3 \rightarrow \mathrm{NH}_3^+ + \mathrm{NH}_3$	1×10^{-9}	est.	
$\mathrm{NH}_3^+ + \mathrm{NH}_3(\mathrm{v}) \rightarrow \mathrm{NH}_3^+ + \mathrm{NH}_3$	1×10^{-9}	est.	-0.1
$\rm NH_3^+ + \rm NO \rightarrow \rm NO^+ + \rm NH_3$	1×10^{-11}	est.	-0.8
Negative ion-neutral collisions	10		
$O^- + H_2 \rightarrow H_2O + e$	7×10^{-10}	62	
$O^- + H_2(v=1) \rightarrow H_2O + e$	7×10^{-10}	est. 62	
$O^- + H_2(v=2) \rightarrow H_2O + e$	7×10^{-10}	est. 62	
$O^- + H_2(v \ge 3) \to H_2O + e$	7×10^{-10}	est. 62	
$O^- + H_2 \rightarrow OH^- + H$	3.3×10^{-11}	62	-0.1
$O^- + H_2(v=1) \rightarrow OH^- + H$	3.3×10^{-11}	est. 62	-0.6
$O^- + H_2(v=2) \rightarrow OH^- + H$	3.3×10^{-11}	est. 62	-1.1
$O^- + H_2(v \ge 3) \rightarrow OH^- + H$	3.3×10^{-11}	est. 62	-1.6
$O^- + H_2O \rightarrow OH^- + OH$	1.4×10^{-9}	62	0.5
$O_2^- + H \rightarrow HO_2 + e$	1.4×10^{-9}	62	
$F^- + H \rightarrow HF + e$	1.6×10^{-9}	69	



Process	Rate coefficient ^b	Reference	ΔH^{b} (eV)
$H^- + H \rightarrow H_2 + e$	1.8×10^{-9}	69	
$H^- + NH_3 \rightarrow NH_2^- + H_2$	8.8×10^{-13}	70	0.3
$H^- + NH_3(v) \rightarrow NH_2^- + H_2$	8.8×10^{-13}	70	0.2
$H^- + N_2O \rightarrow OH^- + N_2$	1.1×10^{-9}	62	-3.7
$OH^- + O \rightarrow HO_2 + e$	2×10^{-10}	62	
$OH^- + H \rightarrow H_2O + e$	1.8×10^{-9}	62	
$NH_2^- + H_2 \rightarrow H^- + NH_2$	2.3×10^{-11}	71	-0.3
$NH_2^- + H_2(v=1) \rightarrow H^- + NH_2$	2.3×10^{-11}	71	-0.8
$NH_2^- + H_2(v=2) \rightarrow H^- + NH_2$	2.3×10^{-11}	71	-1.3
$NH_2^2 + H_2(v \ge 3) \rightarrow H^- + NH_3$	2.3×10^{-11}	71	-1.8
Ion ion neutralization			
$E^- + H O^+ \rightarrow E + H O$	2×10^{-7}	ost 20 ¹	10.1
$F^{-} + OH^{+} \rightarrow F + OH$	2×10^{-7}	est. 29	-10.1
$F^+ \cup H^+ \to F^+ \cup H$	2×10^{-7}	est.	-0.1
$F + \Pi_2 \rightarrow F + \Pi_2$	2×10	est.	
$F + H^{+} \rightarrow F + H$	2×10^{-7}	est.	1.0
$F + NH_3 \rightarrow F + NH_2 + H$	2×10^{-7}	est.	-1.9
$F^- + NH_2^+ \rightarrow F + NH + H$	2×10^{-7}	est.	-1
$F^- + NH^+ \rightarrow F + NH$	2×10^{-7}	est.	-0.6
$F^- + HF^+ \rightarrow F + H + F$	2×10^{-7}	est.	-6.7
$O^- + H_2O^+ \rightarrow O + H_2O$	2×10^{-7}	est.	-12
$O^- + OH^+ \rightarrow O + OH$	2×10^{-7}	est.	-0.5
$O^- + H_2^+ \rightarrow O + H_2$	2×10^{-7}	est.	
$O^- + H^+ \rightarrow O + H$	2×10^{-7}	est.	
$O^- + NH_3^+ \rightarrow O + NH_2 + H$	2×10^{-7}	est.	-1.6
$O^- + NH_2^+ \rightarrow O + NH + H$	2×10^{-7}	est.	-1.7
$O^- + NH^+ \rightarrow O + NH$	2×10^{-7}	est.	-2.5
$O^- + HF^+ \rightarrow O + H + F$	2×10^{-7}	est	-8.6
$O_2^+ + H_2O^+ \rightarrow O_2^- + H_2O_1^-$	2×10^{-7}	est	-13
$O_2^+ + OH^+ \rightarrow O_2^+ + OH$	2×10^{-7}	est.	15
$O_2^+ + O_1^+ \rightarrow O_2^+ + O_1^-$	2×10^{-7}	cst.	
$O_2 + \Pi_2 \rightarrow O_2 + \Pi_2$	2×10^{-7}	cst.	
$O_2 + \Pi \rightarrow O_2 + \Pi$	2×10^{-7}	est.	26
$O_2 + N\Pi_3 \rightarrow O_2 + N\Pi_2 + \Pi$	2×10^{-7}	est.	-2.6
$O_2 + NH_2 \rightarrow O_2 + NH + H$	2×10^{-7}	est.	-2.7
$O_2 + NH^* \rightarrow O_2 + NH$	2×10^{-7}	est.	-3.5
$O_2 + HF' \rightarrow O_2 + H + F$	2×10^{-7}	est.	-9.6
$O_3^- + H_2O^+ \rightarrow O_3 + H_2O$	2×10^{-7}	est.	-11.4
$O_3^- + OH^+ \rightarrow O_3 + OH$	2×10^{-7}	est.	
$O_3^- + H_2^+ \rightarrow O_3 + H_2$	2×10^{-7}	est.	-0.1
$O_3^- + H^+ \rightarrow O_3 + H$	2×10^{-7}	est.	-1.3
$O_3^- + NH_3^+ \rightarrow O_3 + NH_2 + H$	2×10^{-7}	est.	-1
$O_3^- + NH_2^+ \rightarrow O_3 + NH + H$	2×10^{-7}	est.	-1.1
$O_3^- + NH^+ \rightarrow O_3 + NH$	2×10^{-7}	est.	-0.9
$O_3^- + HF^+ \rightarrow O_3 + H + F$	2×10^{-7}	est.	-8
$H^- + F_2^+ \rightarrow H + F_2^*$	$5 \times 10^{-8} \text{ T}_{\text{p}}^{-1/2}$	est. 72	-1.1
$H^- + F^+ \rightarrow H + F^*$	2×10^{-7}	est	
$H^- + N^+_2 \rightarrow H + N^* + N^*$	2×10^{-7}	est	-0.2
$H^- + N^+ \rightarrow H + N^*$	2×10^{-7}	est.	0.2
$H^- + \Omega^+ \rightarrow H + \Omega^*$	2×10^{-7}	oct	
$H^- + O^+ \rightarrow H + O^*$	2×10^{-7}	cot.	
$H^{-} + NE^{+} \rightarrow H + NE \rightarrow E$	2×10 2×10^{-7}	cst.	10.1
$11 \pm 10\Gamma_3 \rightarrow 11 \pm 10\Gamma_2 \pm \Gamma$	2 X 10	est.	-10.1



Process	Rate coefficient ^b	Reference	ΔH^{b} (eV)
$H^- + NF_2^+ \rightarrow H + NF + F$	2×10^{-7}	est.	-5.2
$H^- + NF^+ \rightarrow H + N^* + F$	2×10^{-7}	est.	-6
$H^- + N_2O^+ \rightarrow H + N_2O$	$2 \times 10^{-7} T_{\rm p}^{-1/2}$	62	-12.1
$H^- + NO^+ \rightarrow H + NO$	2×10^{-7}	est.	-0.2
$H^- + H_2O^+ \rightarrow H + H_2O$	2×10^{-7}	est.	-12.7
$H^- + OH^+ \rightarrow H + OH$	2×10^{-7}	est.	-1.2
$H^- + H_2^+ \rightarrow H + H_2$	2×10^{-7}	est.	
$H^- + H^+ \rightarrow H + H^-$	2×10^{-7}	est.	-0.1
$H^- + NH_3^+ \rightarrow H + NH_2 + H$	2×10^{-7}	est.	-2.3
$H^- + NH_2^+ \rightarrow H + NH + H$	2×10^{-7}	est.	-2.4
$H^- + NH^+ \rightarrow H + NH$	2×10^{-7}	est.	-3.2
$H^- + HF^+ \rightarrow H + H + F$	2×10^{-7}	est.	-9.3
$H^- + N_2O^+ \rightarrow H + N_2 + O$	1×10^{-7}	62	-10.3
$OH^- + F_2^+ \rightarrow OH + F_2^*$	2×10^{-7}	est.	-1
$OH^- + F^+ \rightarrow OH + F^*$	2×10^{-7}	est.	-0.8
$OH^- + N_2^+ \rightarrow OH + N_2^*$	2×10^{-7}	est.	-0.9
$OH^- + N^+ \rightarrow OH + N^*$	2×10^{-7}	est.	-0.3
$OH^- + O_2^+ \rightarrow OH + O_2^*$	$2 \times 10^{-7} \mathrm{T_p}^{-1/2}$	73	-0.8
$OH^- + O^+ \rightarrow OH + O^*$	$1 \times 10^{-7} T_{\rm p}^{-1/2}$	73	-0.8
$OH^- + NF_3^+ \rightarrow OH + NF_2 + F$	2×10^{-7}	est.	-9.1
$OH^- + NF_2^+ \rightarrow OH + NF + F$	2×10^{-7}	est.	-4.2
$OH^- + NF^+ \rightarrow OH + N^* + F$	2×10^{-7}	est.	-5
$OH^- + N_2O^+ \rightarrow OH + N_2O$	$2 \times 10^{-7} T_{\rm p}^{-1/2}$	62	-11.1
$OH^- + NO^+ \rightarrow OH + NO$	2×10^{-7}	est.	-1
$OH^- + H_2O^+ \rightarrow OH + H_2O$	2×10^{-7}	est.	-11.7
$OH^- + OH^+ \rightarrow OH + OH$	2×10^{-7}	est.	-0.2
$OH^- + H_2^+ \rightarrow OH + H_2$	2×10^{-7}	est.	-0.4
$OH^- + H^+ \rightarrow OH + H$	2×10^{-7}	est.	-1.6
$OH^- + NH_3^+ \rightarrow OH + NH_2 + H$	2×10^{-7}	est.	-1.3
$OH^- + NH_2^+ \rightarrow OH + NH + H$	2×10^{-7}	est.	-1.4
$OH^- + NH^+ \rightarrow OH + NH$	2×10^{-7}	est.	-1.2
$OH^- + HF^+ \rightarrow OH + H + F$	2×10^{-7}	est.	-8.3
$OH^- + N_2O^+ \rightarrow OH + N_2 + O$	1×10^{-7}	62	-9.3
$NH_2^- + F_2^+ \rightarrow NH_2 + F_2^*$	2×10^{-7}	est.	-1.1
$NH_2^- + F^+ \rightarrow NH_2 + F^*$	2×10^{-7}	est.	
$NH_2^- + N_2^+ \rightarrow NH_2 + N^* + N^*$	2×10^{-7}	est.	-0.2
$NH_2^- + N^+ \rightarrow NH_2 + N^*$	2×10^{-7}	est.	
$NH_2^- + O_2^+ \rightarrow NH_2 + O_2^*$	2×10^{-7}	est.	
$NH_2^- + O^+ \rightarrow NH_2 + O^*$	2×10^{-7}	est.	
$NH_2^- + NF_2^+ \rightarrow NH_2 + NF_2 + F$	2×10^{-7}	est.	-10.1
$NH_2^- + NF_2^+ \rightarrow NH_2 + NF_2 + F$	2×10^{-7}	est.	-5.2
$NH_2^- + NF^+ \rightarrow NH_2 + N^* + F$	2×10^{-7}	est.	-6
$NH_2^- + N_2O^+ \rightarrow NH_2 + N_2O$	$2 \times 10^{-7} \text{ T}^{-1/2}$	est. 62	-12.1
$NH_2^- + NQ^+ \rightarrow NH_2 + NQ$	2×10^{-7}	est	-0.2
$NH_2^- + H_2O^+ \rightarrow NH_2 + H_2O$	2×10^{-7}	est	-12.7
$NH_2^- + OH^+ \rightarrow NH_2 + OH$	2×10^{-7}	est	-1.2
$NH_2^- + H_2^+ \rightarrow NH_2 + H_2$	2×10^{-7}	est	1,2
$NH_{2}^{-} + H^{+} \rightarrow NH_{2} + H$	2×10^{-7}	est	-01
$NH_{2}^{-} + NH_{2}^{+} \rightarrow NH_{2} + NH_{2} + H$	2×10^{-7}	est	-2.3
$NH_2^- + NH_2^+ \rightarrow NH_2 + NH + H$	2×10^{-7}	est.	-2.4
			2.1

Process	Rate coefficient ^b	Reference	ΔH^{b} (eV)
$\overline{\mathrm{NH}_{2}^{-} + \mathrm{NH}^{+}} \rightarrow \mathrm{NH}_{2} + \mathrm{NH}$	2×10^{-7}	est.	-3.2
$NH_2^- + HF^+ \rightarrow NH_2 + H + F$	2×10^{-7}	est.	-9.3
$NH_2^- + N_2O^+ \rightarrow NH_2 + N_2 + O$	1×10^{-7}	est. 62	-10.3
V-V process			
$HF(v=1) + HF(v=1) \rightarrow HF(v \ge 2) + HF$	4.7×10^{-11}	74	
$HF(v=1) + H_2 \rightarrow HF + H_2(v=1)$	$7.4 \times 10^{-13} T_n^{1/2}$	55	
$HF(v \ge 2) + H_2 \rightarrow HF(v = 1) + H_2(v = 1)$	$7.4 \times 10^{-13} T_n^{1/2}$	est. 55	
$HF(v = 1) + N_2 \rightarrow HF + N_2(v)$	4×10^{-15}	74	-0.2
$HF(v \ge 2) + N_2 \rightarrow HF(v = 1) + N_2(v)$	2.5×10^{-14}	74	-0.2
$HF(v = 1) + O_2 \rightarrow HF + O_2(v)$	1.4×10^{-15}	74	-0.3
$HF(v \ge 2) + O_2 \rightarrow HF(v = 1) + O_2(v)$	1×10^{-14}	74	-0.3
$HF(v = 1) + NH_3 \rightarrow HF + NH_3(v)$	1.9×10^{-10}	74	-0.4
$HF(v \ge 2) + NH_3 \rightarrow HF(v = 1) + NH_3(v)$	1.9×10^{-10}	est. 74	-0.4
$H_2(v=1) + HF \rightarrow H_2 + HF(v=1)$	1.9×10^{-12}	74	
$H_2(v = 1) + HF(v = 1) \rightarrow H_2 + HF(v \ge 2)$	7.8×10^{-12}	74	
$H_2(v=2) + HF \rightarrow H_2(v=1) + HF(v=1)$	1.9×10^{-12}	est. 74	
$H_2(v=2) + HF(v=1) \rightarrow H_2(v=1) + HF$	7.8×10^{-12}	est. 74	
$(v \ge 2)$			
$H_2(v \ge 3) + HF \rightarrow H_2(v = 2) + HF(v = 1)$	1.9×10^{-12}	est. 74	
$H_2(v \ge 3) + HF(v = 1) \rightarrow H_2(v = 2) + HF$	7.8×10^{-12}	est. 74	
$(v \ge 2)$			
Neutral-neutral collisions			
$H_2 + F \rightarrow H + HF(v = 1)$	$1.12 \times 10^{-11} T_n^{1/2} \exp(-299/T_g)$	32	-0.9
$H_2(v=1) + F \rightarrow H + HF(v=1)$	$1.12 \times 10^{-11} T_n^{1/2}$	est. 32	-1.4
$H_2(v=2) + F \rightarrow H + HF(v=1)$	$1.12 \times 10^{-11} T_n^{1/2}$	est. 32	-1.9
$H_2(v \ge 3) + F \rightarrow H + HF(v = 1)$	$1.12 \times 10^{-11} T_n^{1/2}$	est. 32	-2.4
$H_2 + F \rightarrow H + HF(v \ge 2)$	$6.34 \times 10^{-11} \text{ T}_{n}^{1/2} \exp(-299/\text{T}_{g})$	32	-0.4
$H_2(v=1) + F \rightarrow H + HF(v \ge 2)$	$6.34 \times 10^{-11} T_n^{1/2}$	est. 32	-0.9
$H_2(v=2) + F \rightarrow H + HF(v \ge 2)$	$6.34 \times 10^{-11} T_n^{1/2}$	est. 32	-1.4
$H_2(v \ge 3) + F \rightarrow H + HF(v \ge 2)$	$6.34 \times 10^{-11} \text{ T}_{n}^{1/2}$	est. 32	-1.9
$H_2 + N \rightarrow NH + H$	$2.66 \times 10^{-10} \exp(-12600/T_g)$	75	1.3
$H_2(v=1) + N \rightarrow NH + H$	$2.66 \times 10^{-10} \exp(-1056/T_{g})$	est. 75	0.8
$H_2(v=2) + N \rightarrow NH + H$	2.66×10^{-10}	est. 75	0.3
$H_2(v \ge 3) + N \rightarrow NH + H$	2.66×10^{-10}	est. 75	-0.2
$H_2 + O \rightarrow OH + H$	$1.6 \times 10^{-11} \exp(-4570/T_g)$	76	0.1
$H_2(v=1) + O \rightarrow OH + H$	1.6×10^{-11}	est. 76	-0.4
$H_2(v=2) + O \rightarrow OH + H$	1.6×10^{-11}	est. 76	-0.9
$H_2(v \ge 3) + O \rightarrow OH + H$	1.6×10^{-11}	est. 76	-1.4
$H_2 + O_2 \rightarrow H + HO_2$	$2.4 \times 10^{-10} \exp(-28\ 500/T_g)$	77	2.3
$H_2(v=1) + O_2 \rightarrow H + HO_2$	$2.4 \times 10^{-10} \exp(-22700/T_g)$	est. 77	1.8
$H_2(v=2) + O_2 \rightarrow H + HO_2$	$2.4 \times 10^{-10} \exp(-16900/T_g)$	est. 77	1.3
$H_2(v \ge 3) + O_2 \rightarrow H + HO_2$	$2.4 \times 10^{-10} \exp(-11\ 100/T_g)$	est. 77	0.8
$H_2 + O_2(v) \rightarrow H + HO_2$	$2.4 \times 10^{-10} \exp(-26 \ 180/T_g)$	est. 77	2.5
$H_2(v=1) + O_2(v) \rightarrow H + HO_2$	$2.4 \times 10^{-10} \exp(-20.380/T_g)$	est. 77	1.6
$H_2(v=2) + O_2(v) \rightarrow H + HO_2$	$2.4 \times 10^{-10} \exp(-14580/T_{o}^{5})$	est. 77	1.1
$H_2(v \ge 3) + O_2(v) \rightarrow H + HO_2$	$2.4 \times 10^{-10} \exp(-8780/T_{o})$	est. 77	0.6
$H_2 + N_2O \rightarrow N_2 + H_2O$	$5.73 \times 10^{-12} T_{\rm p}^{1/2}$	78	-3.4
$H_2(v=1) + N_2O \rightarrow N_2 + H_2O$	$5.73 \times 10^{-12} T_{n}^{1/2}$	est. 78	-3.9
$H_2(v=2) + N_2O \rightarrow N_2 + H_2O$	$5.73 \times 10^{-12} T_{n}^{1/2}$	est. 78	-4.4
$H_2(v \ge 3) + N_2O \rightarrow N_2 + H_2O$	$5.73 \times 10^{-12} T_{n}^{1/2}$	est. 78	-4.9

Process	Rate coefficient ^b	Reference	ΔH^{b} (eV)
$H_2 + OH \rightarrow H_2O + H$	$7.7 \times 10^{-12} \exp(-2100/T_{\sigma})$	77	-0.6
$H_2(v=1) + OH \rightarrow H_2O + H$	7.7×10^{-12}	est. 77	-1.1
$H_2(v=2) + OH \rightarrow H_2O + H$	7.7×10^{-12}	est. 77	-1.6
$H_2(v \ge 3) + OH \rightarrow H_2O + H$	7.7×10^{-12}	est. 77	-2.1
$H_2 + HO_2 \rightarrow H_2O_2 + H$	$5 \times 10^{-11} \exp(-13 \ 100/T_g)$	77	0.9
$H_2(v=1) + HO_2 \rightarrow H_2O_2 + H$	$5 \times 10^{-11} \exp(-7300/T_{g})$	est. 77	0.4
$H_2(v=2) + HO_2 \rightarrow H_2O_2 + H$	$5 \times 10^{-11} \exp(-1500/T_g)$	est. 77	-0.1
$H_2(v \ge 3) + HO_2 \rightarrow H_2O_2 + H$	5×10^{-11}	est. 77	-0.6
$H_2 + NH_2 \rightarrow H + NH_3$	$2.09 \times 10^{-12} \exp(-4277/T_{\sigma})$	79	-0.2
$H_2(v=1) + NH_2 \rightarrow H + NH_3$	2.09×10^{-12}	est. 79	-0.7
$H_2(v=2) + NH_2 \rightarrow H + NH_3$	2.09×10^{-12}	est. 79	-1.2
$H_2(v \ge 3) + NH_2 \rightarrow H + NH_3$	2.09×10^{-12}	est. 79	-1.7
$H + F_2 \rightarrow F + HF$	$1.46 \times 10^{-12} \exp(-1207/T_{\sigma})$	31, 80	-4.3
$H + F_2 \rightarrow F + HF(v = 1)$	$4.38 \times 10^{-12} \exp(-1207/T_{\sigma})$	31, 80	-3.8
$H + F_2 \rightarrow F + HF(v \ge 2)$	$1.4 \times 10^{-10} \exp(-1207/T_g)$	31, 80	-3.3
$H + N_2 \rightarrow NH + N$	$5.27 \times 10^{-10} \text{ T}_{n}^{1/2} \exp(-74280/\text{T}_{g})$	31, 81	6.5
$H + N_2(v) \rightarrow NH + N$	$5.27 \times 10^{-10} \text{ T}_{n}^{1/2} \exp(-70.800/\text{T}_{g})$	81	6.2
$H + O_2 \rightarrow OH + O$	$1.65 \times 10^{-9} T_{\rm p}^{-0.9} \exp(-8750/T_{\rm g})$	77	0.7
$H + O_2(v) \rightarrow OH + O$	$1.65 \times 10^{-9} T_n^{-0.9} \exp(-6430/T_g)$	77	0.5
$H + O_3 \rightarrow OH + O_2$	$1.4 \times 10^{-10} \exp(-480/T_g)$	82	-3.4
$H + FO \rightarrow HF + O$	8.2×10^{-12}	83	-3.6
$H + FO \rightarrow OH + F$	1.58×10^{-11}	83	-2.2
$H + N_2O \rightarrow NO + NH$	$4.96 \times 10^{-7} \text{ T}_{n}^{-2.16} \exp(-18\ 700/\text{T}_{g})$	84	-2.3
$H + N_2O \rightarrow OH + N_2$	$5.13 \times 10^{-14} T_n^{3.15} exp(-3603/T_g)$	84	-2.8
$H + NO_2 \rightarrow OH + NO$	1.28×10^{-10}	85	-1.3
$H + NF_3 \rightarrow HF + NF_2$	$1 \times 10^{-9} \exp(-6640/T_g)$	86	-3.5
$H + NF_2 \rightarrow HF + NF$	$1.36 \times 10^{-11} \exp(-73/T_g)$	30, 87	-2.9
$H + NF_2 \rightarrow HF(v = 1) + NF$	$0.42 \times 10^{-11} \exp(-73/T_g)$	30, 87	-2.4
$H + NF_2 \rightarrow HF(v \ge 2) + NF$	$0.13 \times 10^{-11} \exp(-73/T_g)$	30, 87	-1.9
$H + NF \rightarrow HF + N$	2.5×10^{-13}	85	-3.1
$H + NH_3 \rightarrow H_2 + NH_2$	$6.54 \times 10^{-13} T_n^{2.76} \exp(-5160/T_g)$	88	0.2
$H + NH_3(v) \rightarrow H_2 + NH_2$	$6.54 \times 10^{-13} T_n^{2.76} \exp(-4001/T_g)$	est. 88	0.1
$H + NH_2 \rightarrow NH + H_2$	$1.05 \times 10^{-10} \exp(-4440/T_g)$	89	-0.4
$H + NH \rightarrow H_2 + N$	$5.98 \times 10^{-11} \exp(-166/T_g)$	90	-1.3
$H + HF \rightarrow H_2 + F$	$3.32 \times 10^{-12} \exp(-17520/T_g)$	91	1.3
$H + HF(v = 1) \rightarrow H_2 + F$	$3.32 \times 10^{-12} \exp(-12.882/T_g)$	est. 91	0.8
$H + HF(v \ge 2) \rightarrow H_2 + F$	$3.32 \times 10^{-12} \exp(-8245/T_g)$	est. 91	0.3
$NH_3 + F \rightarrow NH_2 + HF$	0.01×10^{-10}	35, 85	-1.1
$NH_3 + F \rightarrow NH_2 + HF(v = 1)$	0.29×10^{-10}	35, 85	-0.6
$NH_3 + F \rightarrow NH_2 + HF(v \ge 2)$	0.61×10^{-10}	35, 85	-0.1
$\rm NH_3 + \rm N^{\star} \rightarrow \rm NH + \rm NH_2$	5×10^{-11}	92	-0.9
$NH_3 + O \rightarrow OH + NH_2$	$1.6 \times 10^{-11} \exp(-3661/T_g)$	93	0.3
$NH_3 + O^* \rightarrow NH_2 + OH$	2.51×10^{-10}	94	-1.6
$NH_3 + NH \rightarrow NH_2 + NH_2$	$5.25 \times 10^{-10} \exp(-13 \ 440/T_g)$	95	0.6
$NH_3(v) + F \rightarrow NH_2 + HF$	0.01×10^{-10}	est. 35, 85	-1.2
$NH_3(v) + F \rightarrow NH_2 + HF(v = 1)$	0.29×10^{-10}	est. 35, 85	-0.7
$NH_3(v) + F \rightarrow NH_2 + HF(v \ge 2)$	$0.61 imes 10^{-10}$	est. 35, 85	-0.2
$\rm NH_3(v) + \rm N^* \rightarrow \rm NH + \rm NH_2$	5×10^{-11}	est. 92	-1
$NH_3(v) + O \rightarrow OH + NH_2$	$1.6 \times 10^{-11} \exp(-2502/T_g)$	est. 93	0.2
$NH_3(v) + O^* \rightarrow NH_2 + OH$	2.51×10^{-10}	est. 94	-1.7
$NH_3(v) + NH \rightarrow NH_2 + NH_2$	$5.25 \times 10^{-10} \exp(-12280/T_g)$	est. 95	0.5



Process	Rate coefficient ^b	Reference	ΔH^{b} (eV)
$NH_2 + N \rightarrow N_2 + H + H$	1.2×10^{-10}	90	-2.3
$NH_2 + O \rightarrow H_2 + NO$	8.3×10^{-12}	96	-3.7
$NH_2 + O \rightarrow NH + OH$	1.16×10^{-11}	96	-0.3
$NH_2 + NO \rightarrow N_2 + H_2O$	$7.92 \times 10^{-13} \exp(-650/T_{\odot})$	93	-5.4
$NH_2 + NO \rightarrow N_2 + H + OH$	$1.08 \times 10^{-13} \exp(-650/T_{g})$	93	-0.2
$NH_2 + NO_2 \rightarrow H_2O + N_2O$	$7.01 \times 10^{-12} \text{ T}_{n}^{-1.44} \exp(-1122/\text{T}_{g})$	97	-3.9
$NH_2 + NH_2 \rightarrow NH_3 + NH$	$8.30 \times 10^{-11} \exp(-5018/T_{g})$	90	-0.6
$NH + N \rightarrow N_2 + H$	4.98×10^{-11}	90	-6.5
$NH + O_2 \rightarrow NO + OH$	$0.42 \times 10^{-12} \exp(-770/T_g)$	93	-2.6
$NH + O_2 \rightarrow NO_2 + H$	$0.42 \times 10^{-12} \exp(-770/T_g)$	93	-1.3
$NH + O_2(v) \rightarrow NO + OH$	0.42×10^{-12}	est. 93	-2.8
$NH + O_2(v) \rightarrow NO_2 + H$	0.42×10^{-12}	est. 93	-1.5
$NH + NO \rightarrow H + N_2O$	3.12×10^{-11}	84	-1.6
$NH + NO \rightarrow N_2 + OH$	4.5×10^{-11}	98	-4.4
$NH + NO_2 \rightarrow OH + N_2O$	$3.5 \times 10^{-13} \exp(1140/T_g)$	84	-2.9
$NH + NH \rightarrow NH_2 + N$	$1.4 \times 10^{-14} T_{\rm p}^{2.89} \exp(1018/T_{\rm g})$	99	-0.9
$NH + NH \rightarrow N_2 + H + H$	1.16×10^{-9}	100	-3.2
$HF + F \rightarrow F_2 + H$	$2.21 \times 10^{-11} \exp(-50.640/T_{o})$	80	4.3
$HF(v=1) + F \rightarrow F_2 + H$	$2.21 \times 10^{-11} \exp(-44.843/T_g)$	est. 80	3.8
$HF(v \ge 2) + F \rightarrow F_2 + H$	$2.21 \times 10^{-11} \exp(-39.046/T_g)$	est. 80	3.3
$HF + O^* \rightarrow OH + F$	1.5×10^{-11}	101	-0.5
$HF(v = 1) + O^* \rightarrow OH + F$	1.5×10^{-11}	est. 101	-1
$HF(v \ge 2) + O^* \rightarrow OH + F$	1.5×10^{-11}	est. 101	-1.5
$HF + OH \rightarrow H_2O + F$	$1 \times 10^{-11} \exp(-12.240/T_{g})$	85	0.7
$HF(v = 1) + OH \rightarrow H_2O + F$	$1 \times 10^{-11} \exp(-6443/T_{o})$	85	0.2
$HF(v \ge 2) + OH \rightarrow H_2O + F$	$1 \times 10^{-11} \exp(-646/T_g)$	85	-0.3
$OH + F \rightarrow O + HF$	1.2×10^{-11}	33, 102	-1.4
$OH + F \rightarrow O + HF(v = 1)$	1.53×10^{-11}	33, 102	-0.9
$OH + F \rightarrow O + HF(v \ge 2)$	0.6×10^{-11}	33, 102	-0.4
$OH + N \rightarrow NO + H$	4.7×10^{-11}	85	-2.1
$OH + N \rightarrow O + NH$	$1.88 \times 10^{-11} T_{\rm n}^{0.1} \exp(-10.675/T_{\rm g})$	96	1.2
$OH + O \rightarrow H + O_2$	3.5×10^{-11}	85	-0.7
$OH + O_2 \rightarrow O + HO_2$	$3.7 \times 10^{-11} \exp(-26\ 500/T_g)$	77	2.2
$OH + O_2(v) \rightarrow O + HO_2$	$3.7 \times 10^{-11} \exp(-24 180/T_g)$	est. 77	2
$OH + O_3 \rightarrow HO_2 + O_2$	$1.9 \times 10^{-12} \exp(-1000/T_g)$	76	-1.9
$OH + N_2O \rightarrow HO_2 + N_2$	$3.69 \times 10^{-13} \exp(-2740/T_g)$	84	-1.3
$OH + NO_2 \rightarrow HO_2 + NO$	$3.03 \times 10^{-11} \exp(-3360/T_g)$	85	0.2
$OH + H \rightarrow O + H_2$	$5.21 \times 10^{-11} T_n^{0.67} \exp(-518/T_g)$	52	-0.1
$OH + NH_3 \rightarrow NH_2 + H_2O$	$3.5 \times 10^{-12} \exp(-923/T_g)$	103	-0.4
$OH + NH_3(v) \rightarrow NH_2 + H_2O$	3.5×10^{-12}	est. 103	-0.5
$OH + NH_2 \rightarrow O + NH_3$	$3.32 \times 10^{-13} \text{ T}_{n}^{0.4} \exp(-250/\text{T}_{g})$	93	-0.3
$OH + NH \rightarrow NO + H_2$	4×10^{-11}	93	-3.4
$OH + NH \rightarrow H_2O + N$	4×10^{-11}	93	-1.9
$OH + OH \rightarrow O + H_2O$	$1.03 \times 10^{-12} \text{ T}_{n}^{1.4} \exp(200/\text{T}_{g})$	77	-0.7
$OH + HO_2 \rightarrow H_2O + O_2$	8×10^{-11}	76	-2.9
$OH + H_2O_2 \rightarrow H_2O + HO_2$	$2.9 \times 10^{-12} \exp(-160/T_g)$	76	-1.5
$HO_2 + F \rightarrow O_2 + HF$	$8.29 \times 10^{-11} T_n^{0.5}$	102	-3.6
$HO_2 + O \rightarrow OH + O_2$	$2.9 \times 10^{-11} \exp(-200/T_g)$	82	-2.2
$\mathrm{HO}_2 + \mathrm{O}_3 \rightarrow \mathrm{OH} + \mathrm{O}_2 + \mathrm{O}_2$	$1.4 \times 10^{-14} \exp(-600/T_g)$	76	-1.1
$HO_2 + NO \rightarrow NO_2 + OH$	8.8×10^{-12}	85	-0.2
$HO_2 + H \rightarrow OH + OH$	$2.8 \times 10^{-10} \exp(-440/T_{\rm g})$	77	-1.5

Process	Rate coefficient ^b	Reference	ΔH^{b} (eV)
$HO_2 + H \rightarrow H_2 + O_2$	$1.1 \times 10^{-10} \exp(-1070/T_{\sigma})$	76	-2.3
$HO_2 + H \rightarrow H_2O + O$	9.4×10^{-12}	76	-2.2
$HO_2 + NH_2 \rightarrow NH_3 + O_2$	1.3×10^{-11}	93	-2.5
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$8.05 \times 10^{-11} T_n^{-1}$	104	-1.4
$HO_2 + H_2O \rightarrow H_2O_2 + OH$	$4.65 \times 10^{-11} \exp(-16.477/T_{o})$	85	1.5
$H_2O + F \rightarrow OH + HF$	0.29×10^{-11}	34, 85	-0.7
$H_2O + F \rightarrow OH + HF(v = 1)$	1.05×10^{-11}	34, 85	-0.2
$H_2O + F \rightarrow OH + HF(v \ge 2)$	0.06×10^{-11}	34, 85	0.3
$H_2O + N \rightarrow NH + OH$	$6.03 \times 10^{-11} \text{ T}_{n}^{1.2} \exp(-19200/\text{T}_{g})$	96	1.9
$H_2O + O \rightarrow OH + OH$	$1.26 \times 10^{-11} T_n^{1.3} exp(-8605/T_g)$	77	0.7
$\mathrm{H_2O} + \mathrm{O^*} \rightarrow \mathrm{OH} + \mathrm{OH}$	2×10^{-10}	92	-1.2
$H_2O + H \rightarrow H_2 + OH$	$5.24 \times 10^{-12} \text{ T}_{n}^{1.9} \exp(-9265/\text{T}_{g})$	77	0.6
$H_2O_2 + F \rightarrow HO_2 + HF$	$4.96 \times 10^{-11} T_n^{0.5}$	102	-2.2
$H_2O_2 + O \rightarrow OH + HO_2$	$1.4 \times 10^{-12} \exp(-2000/T_g)$	77	-0.8
$\mathrm{H_2O_2} + \mathrm{O^*} \rightarrow \mathrm{O_2} + \mathrm{H_2O}$	5.2×10^{-10}	84	-5.6
$H_2O_2 + O_2 \rightarrow HO_2 + HO_2$	$9 \times 10^{-11} \exp(-19.965/T_g)$	77	1.4
$H_2O_2 + O_2(v) \rightarrow HO_2 + HO_2$	$9 \times 10^{-11} \exp(-17.645/T_g)$	est. 77	1.2
$H_2O_2 + H \rightarrow H_2O + OH$	$4 \times 10^{-11} \exp(-2000/T_g)$	77	-3
$\mathrm{H_2O_2} + \mathrm{H} \rightarrow \mathrm{HO_2} + \mathrm{H_2}$	$8 \times 10^{-11} \exp(-4000/T_g)$	77	-0.9
High temperature chemistry	10		
$H_2 + M \rightarrow H + H + M$	$3.64 \times 10^{-10} \exp(-48.226/T_g)$	90	4.6
$H_2(v=1) + M \rightarrow H + H + M$	$3.64 \times 10^{-10} \exp(-42.426/T_g)$	est. 90	4.1
$H_2(v=2) + M \rightarrow H + H + M$	$3.64 \times 10^{-10} \exp(-36.626/T_g)$	est. 90	3.6
$H_2(v \ge 3) + M \to H + H + M$	$3.64 \times 10^{-10} \exp(-30.826/T_g)$	est. 90	3.1
$H_2^* + M \rightarrow H + H + M$	3.64×10^{-10}	est. 90	-9.1
$NH_3 + M \rightarrow NH_2 + H + M$	$3.65 \times 10^{\circ} \exp(-46.970/T_g)$	105	4.8
$NH_3(v) + M \rightarrow NH_2 + H + M$	$3.65 \times 10^{\circ} \exp(-45.811/T_g)$	est. 105	4.7
$NH_3 + M \rightarrow H_2 + NH + M$	$3.65 \times 10^{-8} \exp(-46.970/1_g)$	est. 105	4.4
$NH_3(V) + M \rightarrow H_2 + NH + M$	$3.65 \times 10^{-6} \exp(-45.811/1_g)$	est. 105	4.3
$NH_2 + M \rightarrow NH + H + M$	$5.91 \times 10^{-1} \ln^{-2} \exp(-45.930/1_g)$	105	4.2
$NH + M \rightarrow N + H + M$	$4.4 \times 10^{-8} \text{ mm}(-3/940/1_g)$	105	3.3
$HF + M \rightarrow H + F + M$	$6.69 \times 10^{-6} I_n^{-1} \exp(-66.225/I_g)$	57	5.9
$HF(v = 1) + M \rightarrow H + F + M$ $HF(v > 2) + M \rightarrow H + F + M$	3.34×10 $I_n \exp(-66.225/I_g)$	57	5.4
$HF(V \ge 2) + M \rightarrow H + F + M$	$2.25 \times 10^{-9} \exp(-60.225/T_g)$	57 77	4.9
$OH + M \rightarrow O + H + M$	$4 \times 10^{-8} \text{ T}^{-1.18} \text{ avp}(-24.260/\text{T})$	77	5.9
$HO_2 + M \rightarrow H + OU + M$	$2.59 \times 10^{-14} \exp(-24.500/T_g)$	ost 106	2.3 5 0
$H_2O + M \rightarrow OH + OH + M$	$5 \times 10^{-7} \exp(-00.289/1_g)$	est. 100	3.2
$H_2O_2 + M \rightarrow OH + OH + M$	$2 \times 10^{-22} 900/1_{g}$	95	2.2
$H + H + M \rightarrow H (y = 1) + M$	4.0×10^{-33}	92 oct 92	-4.0
$H + H + M \rightarrow H_2(v = 1) + M$	4.0×10 4.8×10^{-33}	est. 92	-4.1
$H + H + M \rightarrow H(y > 2) + M$	4.0×10^{-33}	oct 92	-5.0
$H + H + M \rightarrow H_2(V \ge J) + M$ $H + H + M \rightarrow H_2^* + M$	$4.8 \times 10^{-33} \exp(-115.505/T)$	est 92	-3.1
$NH_{+} + H + M \rightarrow NH_{+} + M$	$4.0 \times 10^{-113} \frac{300}{10} \frac{1}{g}$	107	-4.8
$NH_2 + H + M \rightarrow NH_2 + M$	65×10^{-38}	107	-4.0 -4.4
$NH_1 + H_2 + M \rightarrow NH_2(y) + M$	1.4×10^{-32}	est 107	-47
$NH + H_2 + M \rightarrow NH_2(v) + M$	6.5×10^{-38}	est 107	-4.7 -4.4
$NH + H + M \rightarrow NH_{2} + M$	2.6×10^{-35}	107	_4 2
$N + H + M \rightarrow NH + M$	2.6×10^{-36}	107	-3.3
$H + F + M \rightarrow HF + M$	2.07×10^{-35}	80	-5.9
$H + F + M \rightarrow HF(v = 1) + M$	2.07×10^{-35}	est. 80	-5.4

Process	Rate coefficient ^b	Reference	ΔH^{b} (eV)
$H + F + M \rightarrow HF(v \ge 2) + M$	2.07×10^{-35}	est. 80	-4.9
$O + H + M \rightarrow OH + M$	1.62×10^{-32}	108	-3.9
$H + O_2 + M \rightarrow HO_2 + M$	5.4×10^{-32}	85	-2.3
$H + OH + M \rightarrow H_2O + M$	$1.19 \times 10^{-30} T_n^{-2.1}$	est. 109	-5.2
$OH + OH + M \rightarrow H_2O_2 + M$	$6.9 \times 10^{-31} T_n^{-0.8}$	82	-2.2

^aThis table is a subset of the mechanism for NF₃/O₂/H₂ plasmas. The reactions that would occur in NF₃/O₂ plasmas are the same as discussed in Ref. 27.

^bRate coefficients have units of cm³ s⁻¹ unless noted. T_e is electron temperature (eV), T_g is gas temperature (K), and T_n is normalized gas temperature $(T_g/300 \text{ K})$. ΔH is the change of enthalpy (eV).

^cRate coefficients are calculated from the electron energy distributions produced by solutions of Boltzmann's equation using electron impact cross sections. The cross section is for the forward reaction. Reverse cross sections are obtained by detailed balance.

^dThe rate of gas heating by elastic collisions is $k_m(3/2)k_B(2m_e/M)(T_e - T_g) eV cm^3/s$ for elastic rate coefficient k_m , electron mass m_e , neutral mass M, and Boltzmann's constant k_B.

^eThe electron impact cross sections for momentum transfer of HF, HF(v = 1), and HF($v \ge 2$) are assumed to be the same as HCl. The electron impact cross sections for dissociation and ionization of HF, HF(v=1), and $HF(v \ge 2)$ are obtained by shifting the corresponding cross sections of HCl to match the thresholds.

⁶The electron impact superelastic cross sections of HF(v = 1), $HF(v \ge 2)$, and $NH_3(v)$ are calculated from detailed balancing.

^gThe electron impact cross sections for elastic scattering of NH₃(v), NH₂, and NH are assumed to be the same as NH₃. The electron impact cross sections for dissociative attachment, dissociation of NH₃(v), NH₂, and NH, and ionization of NH₃(v) are obtained by shifting the corresponding cross sections of NH₃ to match the thresholds.

^hThe electron impact cross section for elastic scattering of OH is assumed to be the same as CO.

ⁱRate coefficient for charge exchange between ions and neutrals was assumed to be 1×10^{-11} cm³s⁻¹ (1×10^{-9} cm³s⁻¹ for resonant charge exchange)²⁸ when measured or calculated data are not available.

 j Rate coefficient for neutralization between positive and negative ions was assumed to be 2×10^{-7} cm³ s⁻¹ (Ref. 29) when measured or calculated data are not available.

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