A Theoretical Study of the N₂ + H₂ Reactive Collisions for High Vibrational and Translational Energies

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Abstract: High translational temperatures appear in the air inside the shock waves layers created by relatively large meteorites, reentry space vehicles, and hypersonic missiles. Under these conditions, reactions between molecular nitrogen and hydrogen are energetically permitted. In the present work, a quasiclassical trajectories study of the N₂(v′) + H₂(v″) reaction for relative translational energies covering the range of translational energy 20.0 ≤ E_tr/kcalmol⁻¹ ≤ 120.0 is presented. In the calculations, several values of vibrational quantum numbers v′ = 0, 4, 6, 8, 10, 12 and v″ = 4, 6, 8, 10, 12 have been considered. To model the interatomic interactions, a six-dimension global potential energy surface for the ground electronic state of N₂H₂ was used. The specific initial state reaction cross-sections and rate coefficients are reported. The energy effects produced by the reaction that could influence the shock wave modeling are here considered. An analysis of the possible impact of these processes under the atmospheric composition is also presented.

Keywords: molecular collisions; quasiclassical trajectories; atmospheric reactions

1. Introduction

Local temperatures in the range of 2000 ≤ T/K ≤ 45,000 can be produced in the Earth’s atmosphere by the movement of relatively large meteorites, reentry space vehicles, and hypersonic missiles and planes [1–4]. For these temperatures, there is a relatively large number of molecules populating vibrationally excited levels. Then, for such conditions, it is necessary to consider the rate constants of different reactive and nonreactive processes involving vibrationally excited species in works devoted to modeling the movement of the already-mentioned artefacts [2,3,5–7]. In particular, the molecular hydrogen, a minor atmospheric constituent (0.000053 mole percent) [8–10], shows small reactivity for relative low translational energies. For example, their rate constants, in collisions with important atmospheric components such as O and OH for reactions:

\[ \text{H}_2 + \text{O} \rightarrow \text{HO} + \text{H}, \]
\[ \text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}, \]

have the values 9 \times 10^{-18} and 6.7 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}^{-1} [11,12] at 298 K, respectively. In turn, the atomic hydrogen is involved in the atmospheric reactions:

\[ \text{H} + \text{HO}_2 \rightarrow \text{HO} + \text{HO} \] (1)
\[ \text{H} + \text{O}_3 \rightarrow \text{HO} + \text{O}_2 \] (2)
\[ \text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \] (3)

with rate constant values of 7.2 \times 10^{-11}, 7.5 \times 10^{-11} and 2.8 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}, respectively, at 298 K [11,12], several orders of magnitude higher. It means, that by replacing...
the molecular hydrogen with atomic hydrogen, it is possible produce a high chemical
impact in the atmosphere.

The reaction between molecular nitrogen and hydrogen has not been previously con-
sidered in technology [13,14] and shock wave [5] simulations, based upon the small value
of the rate constant for temperature below 5000 K. Nevertheless, preliminary calculations
show relatively high values of the rate coefficients for such a reaction at temperatures above
6000 K [15]. Moreover, the hydrogen atoms produced from title collisions could enter the
important reactions (1)–(3) included in the atmospheric ozone cycles [8]. Furthermore, due
to the high energy barrier involved, the title reactive collisions could influence the energy
balance of the gas. Although an increase in the H$_2$ dissociation with the vibrational energy
is expected, it is not clear how the formation of atomic hydrogen could be affected by the
competition with other reactive and nonreactive channels, which also may be stimulated
by the participation of vibrationally excited H$_2$ molecules.

Thus, the major goal of the present work is to report a detailed theoretical study of
the reaction between molecular hydrogen and nitrogen at their corresponding ground
electronic states, for several initial vibrationally excited combinations. For such a task, the
quasiclassical trajectory (QCT) method and the single-valued double many-body expansion
(DMBE) potential energy surface for the electronic ground state of H$_2$N$_2$ are used. The
paper is organized as follows: Section 2 provides a brief survey of the H$_2$N$_2$ DMBE
potential energy surface together with details of the computational method. The results are
presented and discussed in Sections 3 and 4, correspondingly, while the major conclusions
are gathered in Section 5.

2. Methodology

To represent the interatomic interaction, a global potential energy surface (PES) for the
singlet ground electronic state of N$_2$H$_2$ is used [16]. This function, depending upon the six
interatomic distances, was constructed within the double many-body expansion [17] and
calibrated to multireference configuration interaction \textit{ab initio} energies [16,18]. Such a PES
was previously used in dynamic studies of the NH + NH reaction [19] and the vibrational
relaxation in nonreactive collisions of H$_2$ and N$_2$ [15]. For the interest of this work, from
the N$_2$H$_2$ DMBE PES, the reaction enthalpies are:

\[
\begin{align*}
N_2 + H_2 &\rightarrow N_2 + H + H \quad \Delta H^0_0 = 103.44 \text{kcal mol}^{-1} \\
&\rightarrow N_2H + H \quad \Delta H^0_0 = 113.01 \text{ kcal mol}^{-1}
\end{align*}
\]

Although all the possible reactive channels were considered in the calculations (see later),
only the above products were obtained in the energy interval covered in this study. Figure 1
shows a contour plot of the PES for the title reaction. Isoenergy lines identifying the output
channels N$_2$H + H and N$_2$ + H + H are also represented. Notice there are direct links
between the reactants and the two product valleys here obtained, without passing through
the four body moiety configuration region. This is also illustrated in Figure 2.

For molecular dynamic calculations, the quasiclassical trajectories method was
used [20,21]. In trajectory calculations, we utilized an adapted version of the VENUS96 [22]
code, coupled to the N$_2$H$_2$ PES and making the appropriate assignment of all possible
reactive channels (see Reference [19]). For the problems of interest, mentioned in the
Introduction, the chosen relative diatom–diatom translational energy covered the range
20.0 \leq E_{tr}/ \text{kcal mol}^{-1} \leq 120.0; while the selected initial vibrational quantum numbers for
N$_2$ and H$_2$ were $\nu' = 0, 4, 6, 8, 10, 12$ and $\nu'' = 4, 6, 8, 10, 12$, respectively. Figure 2 depicts a
relaxed reaction path from the interaction potential together with the vibrational energy
levels here considered. The corresponding energies for some combination of both reactants
vibrationally excited were also included.
Figure 1. Contour plot of the DMBE N$_2$H$_2$ PES for the N$_2$ + H$_2$ reaction (black lines). The N–N bond distance, the NNH, and the NHH angles are partially relaxed. Red line contours stand for the N$_2$ + H + H dissociation limit, while blue line contours correspond to the N$_2$H + H channel.

Figure 2. Energetics of a partially relaxed reaction path. Vibrational levels of the reactants and some combinations of both reactants vibrationally excited are also represented.

Additional calculations for translational energies in the interval 140.0 ≤ E$_{tr}$/kcal mol$^{-1}$ ≤ 200.0 were also carried out for combinations $v'' = 4, v' = 4; v'' = 4, v' = 6$ and $v'' = 5, v' = 4$ to improve the fitting of the excitation functions. Exploratory calculations were also carried with one or both reactants rotationally excited. Changes produced in the reaction probability due to the rotational effects are similar to the corresponding increase in translational energy. This subject will be addressed in future studies. Here, the initial rotational quantum numbers of the collision partners were fixed at the ground level $j' = j'' = 0$ and are omitted heretofore.

The determination of the step size for numerical integration was performed by trial and error based on accuracy requirements. A value of $1.0 \times 10^{-16}$ s was found to be sufficient to warrant the conservation of energy to more than 1 part in $10^5$. In turn, the
diatomic–diatomic initial separation was fixed at 15 Å, a value sufficiently large to make the interaction negligible. In turn, the maximum impact parameter $b_{\text{max}}$, which leads to the $r$ reactive channel [23], was obtained following the usual procedure by computing batches of 800 trajectories for fixed values of $b$ [15,19,24] and decreasing its value until a reactive trajectory was obtained. This procedure should allow for accuracy in $b_{\text{max}}$ of about 0.1 Å; the calculated values are reported in Table 1. Batches of 10,000 trajectories were then carried out for each translational energy and vibrational combination. Such a number of trajectories were found to be enough to yield reactive cross-sections with an error of typically a few percent.

Table 1. Summary of the trajectory calculations for the reactive collisions $\text{H}_2(v'') + \text{N}_2(v') \rightarrow \text{N}_2 + \text{H} + \text{H}$ within the IVEQMT approach. $b_{\text{max}}$ in Å. Translational energies ($E_{\text{tr}}$) are given in kcal mol$^{-1}$. The symbol “-” indicates reactive channels remain closed.

| $E_{\text{tr}}$ | $v''$ | $v'$ | $b_{\text{max}}$ | $N_T$ | $N_r$ | $v''$ | $v'$ | $b_{\text{max}}$ | $N_T$ | $N_r$ |
|----------------|-------|------|------------------|------|------|-------|------|------------------|------|------|
| 70.0           | 4     | 4    | -                | -    | -    | 4     | 6    | -                | -    | -    |
| 80.0           | -     | -    | -                | -    | -    | -     | -    | -                | -    | -    |
| 90.0           | -     | -    | -                | -    | -    | 1.0   | 9996 | 27               |
| 100.0          | 1.1   | 9986 | 43               | 1.1  | 9984 | 76    |
| 110.0          | 1.1   | 9980 | 119              | 1.4  | 9982 | 128   |
| 120.0          | 1.4   | 9970 | 182              | 1.5  | 9980 | 249   |
| 70.0           | 4     | 8    | -                | -    | -    | 4     | 10   | -                | -    | -    |
| 80.0           | -     | -    | -                | -    | -    | -     | -    | 0.5              | 9993 | 73   |
| 90.0           | 0.8   | 9986 | 74               | 1.1  | 9990 | 71    |
| 100.0          | 1.1   | 9985 | 110              | 1.1  | 9982 | 205   |
| 110.0          | 1.6   | 9977 | 131              | 1.6  | 9971 | 193   |
| 120.0          | 1.5   | 9971 | 314              | 1.5  | 9974 | 388   |
| 40.0           | 4     | 12   | -                | -    | -    | 8     | 0    | 1.6              | 9846 | 182  |
| 50.0           | -     | -    | -                | -    | -    | -     | -    | 2.0              | 9786 | 456  |
| 60.0           | -     | -    | -                | -    | -    | 2.3   | 9944 | 710              |
| 70.0           | 0.4   | 9999 | 25               | 2.4  | 9674 | 890   |
| 80.0           | 0.7   | 9997 | 74               | 2.6  | 9664 | 937   |
| 90.0           | 1.1   | 9991 | 92               | 2.7  | 9660 | 1048  |
| 100.0          | 0.9   | 9976 | 363              | 2.5  | 9537 | 1387  |
| 110.0          | 1.4   | 9977 | 311              | 2.6  | 9509 | 1459  |
| 120.0          | 1.5   | 9973 | 453              | 2.6  | 9460 | 1616  |
| 30.0           | 8     | 4    | -                | -    | -    | 8     | 6    | 0.6              | 10,000 | 7   |
| 40.0           | 2.2   | 10,000| 412             | 2.2  | 10,000| 405  |
| 50.0           | 2.3   | 9999 | 752              | 2.4  | 10,000| 723  |
| 60.0           | 2.4   | 9999 | 952              | 2.5  | 9999 | 902   |
| 70.0           | 2.5   | 9998 | 1139             | 2.5  | 10,000| 1163 |
| 80.0           | 2.5   | 9997 | 1330             | 2.6  | 9995 | 1258  |
| 90.0           | 2.6   | 9989 | 1436             | 2.6  | 9988 | 1469  |
| 100.0          | 2.7   | 9982 | 1572             | 2.6  | 9987 | 1726  |
| 110.0          | 2.6   | 9980 | 1830             | 2.6  | 9977 | 1946  |
| 120.0          | 2.6   | 9980 | 1830             | 2.6  | 9977 | 1946  |
| 30.0           | 8     | 8    | 0.6              | 10,000| 13   | 8     | 10   | 1.1              | 10,000| 12   |
| 40.0           | 2.2   | 10,000| 429             | 2.1  | 10,000| 488  |
| 50.0           | 2.4   | 10,000| 711             | 2.4  | 10,000| 716  |
| 60.0           | 2.5   | 10,000| 929             | 2.5  | 10,000| 936  |
| 70.0           | 2.5   | 9999 | 1167             | 2.5  | 10,000| 1173 |
| 80.0           | 2.7   | 9998 | 1224             | 2.7  | 9997 | 1256  |
| 90.0           | 2.6   | 9996 | 1530             | 2.8  | 9998 | 1335  |
| 100.0          | 2.7   | 9988 | 1623             | 2.7  | 9991 | 1709  |
| 110.0          | 2.7   | 9975 | 1880             | 2.7  | 9989 | 1937  |
The specific initial-state reactive cross-section for the channel $r$ is calculated as:

$$\sigma_r(E_{tr}; v', v'') = \pi b_{max}^2 \frac{N_r}{N_T}, \quad (6)$$

with the corresponding uncertainties:

$$\Delta \sigma_r = \left( \frac{N_T - N_r}{N_T N_r} \right)^{1/2} \sigma_r \quad (7)$$

where $N_r$ is the number of trajectories ending in the corresponding configurations for products $r$ in a total $N_T$. For a given energetic combination of reactants, the reactive cross-section and the corresponding error for a specific output channel were calculated from relations (6) and (7). In this work, we adopted the following numerical criteria: when the obtained value of $\sigma_r$ is smaller than seven times its corresponding error, the cross-section is negligibly small and the channel is considered as closed.

From the specific initial-state reactive cross-section and assuming a Maxwell–Boltzmann distribution over the translational energy $E_{tr}$, the specific initial-state reactive thermal rate coefficients are obtained as

$$k(T; v', v'') = g_r(T) \left( \frac{2}{k_B T} \right)^{3/2} \left( \frac{1}{\pi \mu} \right)^{1/2} \int E_{tr} \sigma_r(E_{tr}; v', v'') e^{-\frac{E_{tr}}{k_B T}} dE_{tr} \quad (8)$$
where \( k_B \) is the Boltzmann constant, \( \mu \) is the reduced mass of the colliding molecules, \( T \) is the temperature in kelvin, and \( g_e(T) \) the electronic degeneracy factor [25,26]. As the electronic states of \( \text{N}_2\text{H}_2 \) and the collision partners are singlets, \( g_e \) assumes the value of 1.

Classical calculations permit molecular systems in configurations with the vibrational energy below their corresponding quantum minimal value or zero-point energy (ZPE). This ZPE leakage of the classical calculations can be eventually corrected after the trajectories integration. In this work, we selected the intermediate vibrational energy quantum mechanical threshold (IVEQMT) [27] to correct the ZPE problem. In the case of the IVEQMT approximation, trajectories ending in products with vibrational energy below a chosen fraction (here, 1/2) of the corresponding ZPE are considered as nonphysical and hence discarded [28]. As the number of rejected trajectories is relatively small, the calculation of new trajectories to replace them can be avoided [28].

3. Results
3.1. Specific Initial-State Reactive Probability and Cross-Section

Table 1 summarized some trajectory results for selected initial states. Within the criteria used to define the closed channels, for the energy range covered in this study, the products formed were only \( \text{N}_2 + \text{H} + \text{H} \) (reaction (4)) and \( \text{N}_2\text{H} + \text{H} \) (reaction (5)). However, for the initial vibrational quantum number of \( \text{H}_2 \) less than or equal to 3, both channels remained closed for all studied relative translational energies, independent of the vibrational energies of the \( \text{N}_2 \), while, in general, the reactive cross-section for \( \text{N}_2\text{H} + \text{H} \) formation was negligible. Thus, except when explicitly mentioned, the following discussion refers to reaction (4).

The calculated values of the specific initial-state reactive cross-section for the \( \text{N}_2 + \text{H} + \text{H} \) formation, according to the IVEQMT approach, are collected in Table 2, while Figure 3 shows the calculated points for the specific initial-state reactive cross-section for the \( \text{N}_2 + \text{H} + \text{H} \) formation vs. translational energy together with the associated error bars for the IVEQMT approximation.

In Figure 3, the vibrational excitation of the \( \text{H}_2 \) molecule increases from Panel (a) to Panel (c) (showing examples of small, middle, and high vibrational excitation for the \( \text{H}_2 \) molecule). Note that the threshold for the reaction (related to the translational energy) decreases and the excitation function increases with the vibrational energy of the \( \text{H}_2 \) molecule (in our calculations, we considered the reactive channel open, when the initial-state reactive cross-section was, at least, 6 times greater than the calculated error). Note also that curves in Panel (a) of Figure 3 have values two orders lower than curves in Panel (c). This means that the level of the reactive cross-section depends on the \( \text{H}_2 \) vibrational excitation.

Table 2. Specific initial-state cross-sections for reaction \( \text{H}_2(\nu'') + \text{N}_2(\nu') \rightarrow \text{N}_2 + \text{H} + \text{H} \) within the IVEQMT approach and the corresponding error, both in \( \text{Å}^2 \). Translational energies (\( E_{tr} \)) are given in kcal mol\(^{-1}\).
Table 2. Cont.

| $v''$ | $v'$ | $E_{tr}$ | $\sigma$ | $\Delta \sigma$ | $v''$ | $v'$ | $E_{tr}$ | $\sigma$ | $\Delta \sigma$ |
|-------|------|---------|--------|--------------|-------|------|---------|--------|--------------|
| 4     | 12   | 40.0    | -      | -            | 8     | 0    | 40.0    | 0.1486 | 0.010        |
| 50.0  |      | 50.0    | -      | -            | 0.5855 | 0.026 |
| 60.0  |      | 60.0    | -      | -            | 1.1866 | 0.043 |
| 70.0  |      | 0.0012  | 0.0002 |              | 70.0  | 1.6647 | 0.053 |
| 80.0  |      | 0.0114  | 0.001  |              | 80.0  | 2.0591 | 0.063 |
| 90.0  |      | 0.0350  | 0.003  |              | 90.0  | 2.4846 | 0.072 |
| 100.0 |      | 0.0925  | 0.004  |              | 100.0 | 2.8555 | 0.070 |
| 110.0 |      | 0.1920  | 0.011  |              | 110.0 | 3.2584 | 0.078 |
| 120.0 |      | 0.3210  | 0.014  |              | 120.0 | 3.6278 | 0.082 |
| 8     | 4    | 50.0    | 0.6264 | 0.030        | 8     | 6    | 50.0    | 0.6158 | 0.029        |
| 60.0  |      | 1.2500  | 0.044  |              | 60.0  | 1.3083 | 0.046 |
| 70.0  |      | 1.7228  | 0.053  |              | 70.0  | 1.7712 | 0.056 |
| 80.0  |      | 2.2368  | 0.062  |              | 80.0  | 2.2835 | 0.062 |
| 90.0  |      | 2.6123  | 0.067  |              | 90.0  | 2.6729 | 0.070 |
| 100.0 |      | 3.0530  | 0.074  |              | 100.0 | 3.1234 | 0.075 |
| 110.0 |      | 3.6067  | 0.083  |              | 110.0 | 3.6703 | 0.080 |
| 120.0 |      | 3.8935  | 0.083  |              | 120.0 | 4.1422 | 0.084 |
| 8     | 8    | 30.0    | 0.0014 | 0.0004       | 8     | 10   | 30.0    | 0.0045 | 0.001        |
| 50.0  |      | 0.6523  | 0.030  |              | 50.0  | 0.6761 | 0.029 |
| 60.0  |      | 1.2866  | 0.046  |              | 60.0  | 1.2956 | 0.046 |
| 70.0  |      | 1.8240  | 0.057  |              | 70.0  | 1.8378 | 0.057 |
| 80.0  |      | 2.2914  | 0.063  |              | 80.0  | 2.3031 | 0.063 |
| 90.0  |      | 2.8037  | 0.075  |              | 90.0  | 2.8773 | 0.075 |
| 100.0 |      | 3.2505  | 0.076  |              | 100.0 | 3.2881 | 0.082 |
| 110.0 |      | 3.7214  | 0.084  |              | 110.0 | 3.9175 | 0.086 |
| 120.0 |      | 4.3164  | 0.089  |              | 120.0 | 4.4410 | 0.090 |
| 8     | 12   | 10.0    | -      | -            | 12    | 0    | 10.0    | 3.1958 | 0.082        |
| 20.0  |      | -      | -      |              | 20.0  | 8.6574 | 0.154 |
| 30.0  |      | 0.0020 | 0.0004 |              | 30.0  | 11.2792 | 0.175 |
| 40.0  |      | -      | -      |              | 40.0  | 12.6985 | 0.189 |
| 50.0  |      | 0.6785 | 0.028  |              | 50.0  | 13.6073 | 0.185 |
| 60.0  |      | 1.3430 | 0.049  |              | 60.0  | 14.0585 | 0.195 |
| 70.0  |      | 1.8555 | 0.057  |              | 70.0  | 14.4943 | 0.197 |
| 80.0  |      | 2.3660 | 0.064  |              | 80.0  | 14.6393 | 0.198 |
| 90.0  |      | 2.9192 | 0.079  |              | 90.0  | 14.8886 | 0.190 |
| 100.0 |      | 3.3957 | 0.087  |              | 100.0 | 14.8748 | 0.190 |
| 110.0 |      | 4.0317 | 0.087  |              | 110.0 | 14.6792 | 0.190 |
| 120.0 |      | 4.5405 | 0.091  |              | 120.0 | 14.8566 | 0.199 |
| 12    | 4    | 10.0    | 3.2911 | 0.090        | 12    | 6    | 10.0    | 3.3056 | 0.090        |
| 30.0  |      | 11.3978 | 0.183  |              | 30.0  | 11.4588 | 0.183 |
| 50.0  |      | 13.8968 | 0.193  |              | 50.0  | 13.9073 | 0.193 |
| 80.0  |      | 15.0690 | 0.197  |              | 80.0  | 15.1252 | 0.186 |
| 100.0 |      | 15.3895 | 0.207  |              | 100.0 | 15.6519 | 0.207 |
| 120.0 |      | 15.3727 | 0.198  |              | 120.0 | 15.4803 | 0.198 |
| 12    | 8    | 10.0    | 3.3164 | 0.087        | 12    | 10   | 10.0    | 3.43036 | 0.092       |
| 30.0  |      | 11.6741 | 0.184  |              | 30.0  | 11.7080 | 0.191 |
| 50.0  |      | 14.1396 | 0.202  |              | 50.0  | 14.1229 | 0.193 |
| 80.0  |      | 15.2055 | 0.179  |              | 80.0  | 15.2489 | 0.188 |
| 110.0 |      | 15.6025 | 0.190  |              | 110.0 | 15.7420 | 0.189 |
| 120.0 |      | 15.5214 | 0.198  |              | 120.0 | 15.7183 | 0.198 |
| 12    | 12   | 10.0    | 3.50514| 0.096        | 30.0  | 11.7666 | 0.184 |
| 50.0  |      | 14.0604 | 0.193  |              | 50.0  | 14.3876 | 0.188 |
| 80.0  |      | 15.7715 | 0.198  |              | 80.0  | 15.6944 | 0.198 |
Figure 3. Specific initial-state reactive cross-section for the N$_2$ + H + H formation considering the reactive collisions H$_2$(v'') + N$_2$(v') inside the IVEQMT approach. In Panel (a) H$_2$(v'' = 4) + N$_2$(v' = 4, 6, 8, 10, 12), in Panel (b) H$_2$(v'' = 8) + N$_2$(v' = 0, 4, 6, 8, 10, 12), and in Panel (c) H$_2$(v'' = 12) + N$_2$(v' = 0, 4, 6, 8, 10, 12).

For v'' ≤ 3, the reactive channel remains closed (the threshold for H$_2$ vibrational energy), inside the considered intervals for the translational energies and vibrational energies of the N$_2$. In the case of H$_2$(v'' = 4, 5), the reaction channel (4) opens for the vibrational quantum numbers of the N$_2$ that satisfy the conditions v' ≥ 4 (determining the total vibrational energy threshold for these cases). The described situation explains the small values of specific initial-state reactive cross-section reported in Panel (a), where
graphics corresponding to vibrational combinations near the mentioned vibrational energy threshold have been shown.

All panels in Figure 3 show that the vibrational excitation of the N\textsubscript{2} molecule leads to small increases in the initial-state reactive cross-section as expected from the great difference between the vibrational quanta of both molecules.

The analytical representation of the initial-state reactive excitation functions for vibrational levels included in Figure 3 follows the function [29]:

\[
\sigma(E_{tr}; v', v'') = f_{E_{tr}, v', v''}(E_{tr} - E_{tr}^{E_{v'}, E_{v''}})n \exp\left(-m_{E_{tr}, v', v''}(E_{tr} - E_{th}^{E_{v'}, E_{v''}})\right),
\]

where the parameters \(f_{E_{tr}, v', v''}\), \(m_{E_{tr}, v', v''}\), \(n\), and \(E_{th}^{E_{v'}, E_{v''}}\) were here expressed as the linear functions of the variable \(E_{v'}\):

\[
f_{E_{tr}, v', v''} = a_0 + a_1(E_{v'} - E_r)
\]

\[
m_{E_{tr}, v', v''} = b_0 + b_1(E_{v'} - E_r)
\]

\[
n = c_0 + c_1(E_{v'} - E_r)
\]

\[
E_{th}^{E_{v'}, E_{v''}} = d_0 + d_1(E_{v'} - E_r),
\]

where \(E_r\) is the vibrational energy of the N\textsubscript{2} used as reference. For Panels (b) and (c), the reference is the energy of the level \(v' = 0\), while in Panel (a), the fitting for the vibrational quantum numbers \(v' = 4, 6, 8\) takes as reference the energy for level \(v' = 4\) and for the case of vibrational quantum number \(v' = 10, 12\), the energy reference corresponds to the level \(v' = 12\).

The coefficients in the linear Equations (10)–(13) are reported in Table S1 of the Supplementary Material (SM). We verified that the model works for all intermediate vibrational excitation of both molecules inside the intervals \(4 \leq v'' \leq 12\) and \(0 \leq v' \leq 12\). Additional figures for the excitation functions of other vibrational combinations were included in the Figure S1 in the SM.

In all cases, the initial-state reactive cross-sections are increasing functions of initial translational and vibrational energies. For higher translational energies, the interactions between molecules during collisions are stronger because they could be closer, while the increase in the initial vibrational energies produces greater deformations of the excited molecule, leading to bigger collision areas and small increases in the quadrupole moment. The competition with other reactive channels produces in all cases the formation of a plateau. The onset of this behavior strongly depends on the vibrational energy of the H\textsubscript{2}. While in Panel (c), it is observed after a translational energy of 60–70 kcal mol\textsuperscript{-1} in Panels (a) and (b), it appears after 140–160 kcal mol\textsuperscript{-1}. Despite the large values of the relative translational energies, the initial-state cross-sections for reaction have relatively small values, corresponding to the nonpolar character of both colliding molecules.

As mentioned in the first paragraph of this section, the reactive channel (5) is also opened with very small probabilities. To make a comparison with the reactive channel (4), the additional trajectories were calculated for H\textsubscript{2}(v'' = 12) + N\textsubscript{2}(v' = 0). The calculated specific initial-state reactive cross-sections are displayed in Figure S4 of the SM. These values are at least 40 times smaller than the corresponding for channel (4) for the same energetic initial conditions. Moreover, as was indicated in [19], the N\textsubscript{2}H molecule, as a rule, immediately produces N\textsubscript{2} + H + H\textsubscript{2}; thus, it is possible to consider the reaction (5) as a slight contribution to the atomic hydrogen formation.

3.2. Energetic Features in the Reactive Molecular Ensemble

The discussion in the previous subsection points out the efficiency of the vibrational excitation of the H\textsubscript{2} molecule to produce the increase in reaction (4). In particular, it was demonstrated that for vibrational quantum numbers \(v'' \geq 6\) of the H\textsubscript{2}, the reaction (4) allows for translational energies greater than a determined value even when the N\textsubscript{2} is in
the ground vibrational state. Under the conditions of the present work, as was shown in Figures 1 and 2, reactive trajectories could also avoid the minimum of the PES and go directly to the products. Thus, calculations for these cases show that the barrier for the reaction (4) is determined by the energy difference between products and reactants in their ground electronic states. In all cases, the H₂ vibrational energy is essentially used to overpass that barrier and break the chemical bond.

Panel (a) of Figure 4 shows the arithmetic means of the energies corresponding to rotational degrees of freedom of the N₂ after reaction (4), while Panel (b) of the same figure reports the difference in the vibrational degrees of freedom of the N₂ in the products of the reaction (4) with their initial values. Finally, Panel (c) shows the difference between the arithmetic mean of the relative translational energy of the products and the value of the initial relative translational energy of reactants.

Panel (a) of Figure 4 shows an increase in the N₂ rotational energy mean value in the interval 0.7 < E\textsubscript{rot,N₂}/kcal mol\(^{-1}\) < 5.25 with the increment of the relative translational energy. Such incremental results are practically independent of the vibrational energy of the molecule; thus, it is determined by the T-R processes. The observed slight increment in the rotational energy of the N₂ with the quantum number v' in the panel is probably due to the variation of inertial molecular properties when the molecular oscillations grow.

From the analysis of Panel (b) of Figure 4, with the exception of the N₂(v' = 0) case (for which it is evident that it only has possibility to increase the vibrational energy), the figure shows a loss in the N₂ vibrational energy in the interval 1.0 < E\textsubscript{vib,N₂}/kcal mol\(^{-1}\) < 13.0. This energy loss is conditioned, principally, by the V-T processes but also includes a small transfer of energy used to break the chemical bond. This transferred energy warrants the small increase in the specific initial-state reactive cross-section with N₂ vibrational energy reported in Figure 3.

Following the previous analysis, one may rationalize that the energy associated with the relative translational degrees of freedom and the vibrational energy of the H₂ are the principal energy sources for the chemical reaction. To carry out an approximated quantitative energy balance, we introduced the following expression obtained from the energy conservation for the different processes discussed above:

\[
E\text{'}\text{int,N₂} - E\text{'}\text{tr} = (E\text{'}\text{vib,H₂} + E\text{'}\text{vib,N₂} - E\text{'B}) - E\text{'}\text{int,N₂}.
\]  
(14)

where \(E\text{'}\text{tr}\) is the initial relative translational energy; \(E\text{'}\text{fr}\) is the arithmetic means of translational energies corresponding to the reactive molecular ensemble after the chemical reaction (4); \(E\text{'}\text{vib,H₂}\) and \(E\text{'}\text{vib,N₂}\) are the initial vibrational energies of the H₂ and N₂ molecules before reaction, respectively; \(E\text{'B}\) is the energy barrier for reaction (4) discussed above; and \(E\text{'}\text{int,N₂}\) is the arithmetic mean of the N₂ internal energy (the sum of vibrational and rotational energies) after reaction (of course, the arithmetic means were obtained from the trajectory calculations reported in the present work).

From Panel (c) of Figure 4, for the considered initial energy conditions, the molecular reactive ensemble experiences a significant cooling. To compare the results in Figure 4 with others obtained for different initial conditions, Figures S2 and S3 were included in the SM. In these figures, similar curves were reported for the initial conditions corresponding to collisions of H₂(v'' = 12) + N₂(v' = 0, 6, 12) (Figure S2) and H₂(v'' = 4) + N₂(v' = 4, 6, 12) (Figure S3). The curves in Figure S2 show that the N₂ experiences a small excitation when it is initially in its ground vibrational state, while in other situations it shows a loss of vibrational energy. In turn, the curves for the rotational degrees of freedom show a higher excitation than those observed in Figure 4 for H₂(v'' = 8). On the other hand, the cooling process reported in the Panels (c) of both figures are less intensive in the case of Figure S2. Moreover, for the collisions H₂(v'' = 12) + N₂(v' = 12), the molecular reactive ensemble is slightly heated.

The comparison of Figure S3 with the other reported cases in Figures 4 and S2 leads to the conclusion that when the reactive processes diminish, the relaxation processes are
more relevant, leading to the highest rotational excitation, a stronger loss of N\textsubscript{2} vibrational energy, and, in general, the heating of the molecular reactive ensemble.

Figure 4. Comparison of the arithmetic mean of energies for different degrees of freedom in the reaction (4) within the IVEQMT approach versus translational energies when the reactants are the H\textsubscript{2} (v''=8) and the N\textsubscript{2} in the vibrational excited states \(v'=0, v'=6, v'=12\). In Panel (a), the mean values of the rotational energy for the product N\textsubscript{2} are displayed. In Panel (b), the differences between the mean values of the vibrational energy for the N\textsubscript{2} after reaction and the corresponding initial value are shown. In Panel (c), the differences between mean values of the relative translational energy of the molecular system after reaction and the corresponding initial values are presented.
3.3. Specific Initial-State Reactive Thermal Rate Coefficients

From the specific initial-state reactive cross-sections Equation (9) and using the integral in Equation (8), one then obtains:

\[
k(T; v', v'') = \left( \frac{8k_B T}{\pi \mu} \right)^{1/2} \int f_{E_{v', v''}} (k_B T)^n \exp \left( -\frac{E_{E_{v', v''}}}{k_B T} \right) \left[ \frac{\Gamma (n + 2) \left(m_{E_{v', v''}} k_B T + 1\right)^{-n+2} \Gamma(n + 1) \left(m_{E_{v', v''}} k_B T + 1\right)^{-n+1}}{k_B T} \right]
\]

for the specific initial-state reactive thermal rate coefficients as a function of the temperature. Here, \( \Gamma(\cdots) \) is the gamma function.

Figure 5 shows the curves of the specific initial-state reactive thermal rate coefficients for the same combinations of vibrational energies used before for the calculations of the corresponding cross-sections within the approaches IVEQMT. As expected from the specific initial-state cross-sections, they are increasing the functions of both vibrational and relative translational energies, and for a fixed vibrational excitation of the H\(_2\), the increase in the N\(_2\) vibrational energy produces only slight growths in the specific initial-state thermal rate coefficients.

Figure 5. Cont.
Figure 5. Specific initial-state reactive thermal rate coefficients for the N$_2$ + H + H formation considering the reactive collisions H$_2$(v'') + N$_2$(v') inside the IVEQMT approach. In Panel (a) H$_2$(v'' = 4), in Panel (b) H$_2$(v'' = 8), and in Panel (c) H$_2$(v'' = 12).

4. Discussion

The analysis conducted in the subsection “Energetic Features in the Reactive Molecular Ensemble” points out that the majority of the initial energy combinations leading to reaction produce a decrease in the translational energy; thus, considering the values of the vibrational average thermal rate coefficients for the reaction (4) here reported, it could be necessary to account for this decrease in the translational energy to calculate the temperature of the gas behind the shock wave in the modeling works devoted to the hypersonic flights.

Figure 6 shows the vibrational average thermal rate coefficients for different situations. The red curves in this figure corresponds to the vibrational average thermal rate coefficients for reaction (4) calculated using the equation

$$< k(T; v', v'') >= \frac{\sum_{v''} \sum_{v'''} \omega_{v''} \omega_{v'''} [k(T; v', v'')] }{\sum_{v''} \sum_{v'''} \omega_{v''} \omega_{v'''}},$$

(16)

where $\omega_{v''}$ and $\omega_{v'''}$ are the vibrational populations of N$_2$ and H$_2$, respectively, while the blue curves represent the vibrational average thermal rate coefficients $2 \times < k(T; v', v'') >$ that determine the temporal variation of the H concentration following the equation:

$$\frac{d[H]}{dt} = 2 \times < k(T; v', v'') > [H_2][N_2].$$

(17)

Both curves experience a very rapid increase until the formation of a high-value plateau after the translational temperature of 15,000 K. Such temperatures, and higher, are obtained in the modeling studies reported in [1-3] for the shock wave produced by hypersonic objects in the atmosphere; thus, the formation of abundant atomic hydrogen considering the high chemical rate predicted by Equation (17) is a real possibility in the air around hypersonic objects.
Figure 6. Calculated vibrational average thermal rate coefficients for studied processes. In Panel (a) for the \( \text{N}_2 + \text{H} + \text{H} \) formation (red curve) and atomic hydrogen formation (blue curve) considering a Boltzmann distribution for the population of vibrationally excited reactants at the calculated temperature. In Panel (b), together with the curves previously described in Panel (a), the vibrational average thermal rate coefficients for atomic hydrogen formation considering thermal disequilibrium conditions for the vibrational populations of reactants are shown (see text for description).

In a recent paper [30], a QCT study of the reaction (18) for a wide range of temperatures \( (300 \leq T/K \leq 20,000) \) was presented. The total rate for the reaction (18) was reported, including also the weighted contribution of the

\[
\text{N}(^4 \text{S}) + \text{O}_2(X^3 \Sigma_g^+) \rightarrow \text{O}(^3 \text{P}) + \text{NO}(X^2 \Pi)
\]  

(18)

\( ^2 \Lambda' \) and \( ^4 \Lambda' \) surfaces. Independently of the quantitative differences which are expected for different systems, the qualitative similarities between the rate constants are remarkable.

As expected, from the rapid expansion of the gas behind the shock wave, high thermal nonequilibrium conditions in the gas layer near the moving objects are reported in the mentioned papers [1–3]. To make a qualitative evaluation of the effect of the disequilibrium conditions on the atomic hydrogen formation, the curves calculated considering the hypothetical hot Boltzmann distribution shifted in 5000 K (brown curve) and 10,000 K (magenta curve) are represented in Panel (b) of the Figure 6. These curves show that, under nonequilibrium conditions, their plateau behavior is retained until the translational temperature around 10,000 K, and the values of the average thermal rate coefficients for
temperatures below 7500 K are, at least, one order of magnitude higher than those obtained under thermal equilibrium conditions. Considering the high values of the average thermal rate coefficients in Equation (16), it is possible to expect the conversion of a considerable quantity of molecular hydrogen in atomic hydrogen that could enter important atmospheric reactions as (1)–(3), leading to a relatively significant atmospheric impact. Finally, we should mention that no comparison with experimental data was possible since, to our knowledge, no such data exist in the literature for the interval of temperature considered in the present work.

5. Conclusions

In this work, we have reported a quasiclassical dynamic study of the \( \text{N}_2(v') + \text{H}_2(v'') \) reaction for several vibrational states of the reactants \((0 \leq v' \leq 12; 0 \leq v'' \leq 12)\) and a wide range of relative translational energy \((20 \leq E_{\text{tr}}/ \text{ kcal mol}^{-1} \leq 120)\). According to our calculation, the most probable product was \( \text{N}_2 + \text{H} + \text{H} \). The formation of \( \text{N}_2\text{H} \) was also observed, with a negligible contribution to total reaction. As expected, the vibrational energy in the \( \text{H}_2 \) molecule has a determinant role in the dissociation process. The initial vibrational energy content in \( \text{N}_2 \) is partially used in dissociating the molecular hydrogen. The reaction excitation functions exhibit typical shapes for barrier-like processes, and the models were correspondingly presented. Specific initial-state thermal rate coefficients and vibrationally averaged rate constants were reported. The relatively high values of these rates for the considered conditions indicate the role of the title reaction in atmospheric issues involving high temperatures might be important, particularly as a source of atomic hydrogen. Of course, such a verification requires considering the reaction in the kinetic models. The energetic analysis of the calculated trajectories points toward a cooling effect when transforming the molecular hydrogen in the dissociated form by collisions with vibrationally excited molecular nitrogen.

Supplementary Materials: The following are available at https://www.mdpi.com/article/10.3390/atmos12101349/s1, Table S1, Figures S1–S4.

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Abbreviations

The following abbreviations are used in this manuscript:

| Abbreviation | Description |
|--------------|-------------|
| PES          | Potential Energy Surface |
| QCT          | Quasiclassical Trajectories |
| IVEQMT       | Intermediate Vibrational Energy Quantum Mechanical Threshold |
| ZPE          | Zero-Point Energy |
| V-T processes| Energy transfer from vibrational to translational degrees of freedom |
| T-R processes| Energy transfer from translational to rotational degrees of freedom |

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