The role of highly vibrationally excited H\(_2\) initiating the nitrogen chemistry

Quantum study and 3\(\sigma\) detection of NH emission in the Orion Bar PDR

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ABSTRACT

The formation of hydrides by gas-phase reactions between H\(_2\) and a heavy element atom is a very selective process. Reactions with ground-state neutral carbon, oxygen, nitrogen, and sulfur atoms are very endoergic and have high energy barriers because the H\(_2\) molecule has to be fragmented before a hydride bond is formed. In cold interstellar clouds, these barriers exclude the formation of CH, OH, NH, and SH radicals through hydrogen abstraction reactions. Here we study a very energetically unfavorable process, the reaction of N\(^{(\ast)}\) atoms with H\(_2\) molecules. We calculated the reaction rate coefficient for H\(_2\) in different vibrational levels, using quantum methods for \(\varepsilon=0–7\) and quasi-classical methods up to \(\varepsilon=12\); for comparison purposes, we also calculated the rate coefficients of the analogous reaction S\(^{(\ast)}\)+H\(_2\)\(\rightarrow\)SH+H. Owing to the high energy barrier, these rate coefficients increase with \(\varepsilon\) and also with the gas temperature. We implemented the new rates in the Meudon photodissociation region (PDR) code and studied their effect on models with different ultraviolet (UV) illumination conditions. In strongly UV-irradiated dense gas (Orion Bar conditions), the presence of H\(_2\) in highly vibrationally excited levels (\(\varepsilon\geq7\)) enhances the NH abundance by two orders of magnitude (at the PDR surface) compared to models that use the thermal rate coefficient for reaction N\(^{(\ast)}\)+H\(_2\)\(\rightarrow\)NH+H. The increase in NH column density, N(NH), across the PDR is a factor of \(\sim25\). We investigate the excitation and detectability of submillimeter NH rotational emission lines. Being a hydride, NH excitation is very subthermal (\(T_{\rm rot}\ll T_{\rm e}\)) even in warm and dense gas. We explore existing Herschel/HIFI observations of the Orion Bar and Horsehead PDRs. We report a 3\(\sigma\) emission feature at the \(\sim974\) GHz frequency of the NH \(J_{11}l_{11}\sim1\rightarrow0\) line toward the Bar. The emission level implies N(NH) \(\sim10^{13}\) cm\(^{-2}\), which is consistent with PDR models using the new rate coefficients for reactions between N and UV-pumped H\(_2\). This formation route dominates over hydrogenation reactions involving the less abundant N\(^+\) ion. JWST observations will quantify the amount and reactivity of UV-pumped H\(_2\) in many interstellar and circumstellar environments.

Key words. ISM: molecules – molecular processes – photon-dominated region (PDR) – line: identification

1. Introduction

The abundances of interstellar hydrides provide key information about the physical conditions where they are found, the H\(_2\)/H fraction, and the ionization rate (Gerin et al. 2016). Much of the interstellar chemistry begins with the reaction of H\(_2\) molecules with a heavy element atom X. The dominant ionization state of X in neutral clouds depends on its ionization potential (IP). Indeed, only far-ultraviolet (FUV) photons with energies below 13.6 eV – that is to say those that cannot ionize hydrogen – penetrate diffuse neutral clouds (Snow & McCall 2006) and the illuminated rims of denser molecular clouds, in other words their photodissociation regions (PDRs; Hollenbach & Tielens 1997; Wolfire et al. 2022). In consequence, the initial gas reservoir is ionized for elements such as C (IP = 11.26 eV) and S (10.36 eV), but neutral\(^1\) for elements such as N (IP = 14.33 eV) and O (13.62 eV).

Even for small amounts of H\(_2\) in the gas, the reaction

\[
X + H_2 \rightarrow XH + H,
\]

\(^1\) The existence of small amounts of O\(^+\) and N\(^+\) ions in these clouds is related to the ionization produced by energetic cosmic-ray particles and X-rays. The presence of abundant C\(^+\) and S\(^+\) ions is generally related to the presence of stellar or secondary FUV photons.

with \(X=X^0\) or \(X^+\) and \(XH=XH^0\) or \(XH^+\), initiates the formation of interstellar hydrides. This happens in diffuse clouds of initially atomic gas (\(n_H \sim 100–500\) cm\(^{-3}\); e.g., Federman et al. 1995; Gerin et al. 2010; Neufeld et al. 2010; Sonnentrucker et al. 2010; Schilke et al. 2014), and in dense PDRs, as demonstrated by the detection of OH, CH, CH\(^+\), SH\(^+\), OH\(^+\), and HF rotational emission lines toward the Orion Bar (Naylor et al. 2010; Goicoechea et al. 2011, 2021; Nagy et al. 2013; van der Tak et al. 2013; Joblin et al. 2018; Kaku et al. 2019).

The rate coefficient of reaction (1) greatly depends on the element X involved (see Sect. 2). If we restrict ourselves to neutral C, N, O, and S, these hydrogen abstraction reactions are very endoergic and have substantial energy barriers. When X is a cation, reaction (1) is endoergic but barrierless. The only exception is X = O\(^+\), for which the reaction is exothermic and thus fast. Indeed, OH\(^+\) is readily detected in interstellar clouds (e.g., Indriolo et al. 2015). In general, the endothermicity of these reactions (\(\Delta E/\hbar\) of several thousand kelvin) is significantly above the bulk gas temperatures in diffuse interstellar clouds (\(T \sim 30–100\) K). In particular, the presence of CH\(^+\) and SH\(^+\) absorption lines toward these low density clouds has always been puzzling (e.g., Godard et al. 2012). Plausible explanations are the formation of these hydrides in hot gas (\(T \sim 1000\) K)
heated by shocks (e.g., Elitzur & Watson 1980; Pineau des Forêts et al. 1986; Drainé & Katz 1986; Neufeld et al. 2002), dissipation of turbulence and ion-neutral drift (Godard et al. 2014), or triggering by the presence of hot \( H_2 \) from phase mixing (Lesaffre et al. 2007; Valdivia et al. 2017). These mechanisms, however, are not relevant in dense molecular clouds and PDRs.

Reaction (1) for \( X = N \) is a very energetically unfavorable process: \( \Delta E / k_B \approx 15 \, 000 \, \text{K} \), and it has a high barrier. Hence, this reaction is not considered to be a relevant formation pathway for NH in diffuse clouds (Godard et al. 2010), despite line absorption observations showing the presence of NH (Meyer & Roth 1991; Crawford & Williams 1997; Persson et al. 2010, 2012).

It has long been suggested that the presence of high densities of FUV-pumped \( H_2 \) in dense PDRs enhances the reactivity of reaction (1); (Stecher & Williams 1972; Freeman & Williams 1982; Tielens & Hollenbach 1985; Sternberg & Dalgarno 1995). The prototypical example is the Orion Bar, a nearly edge-on rim of the Orion cloud (Tielens et al. 1993; Goicoechea et al. 2016). FUV-pumping in the Lyman and Werner bands of \( H_2 \), followed by radiative or collisional de-excitation, populates \( H_2 \) in highly vibrationally excited levels within the ground-electronic state (Black & Dalgarno 1976; Sternberg & Dalgarno 1989; Burton et al. 1990). Infrared ro-vibrational lines from these very excited levels are readily detected in PDRs (Kaplan et al. 2021).

In order to treat the increase in reactivity of vibrationally excited \( H_2 \), early PDR models assumed state-specific rate coefficients in which the energy \( E_v \) of each \( H_2 \) vibrational state \( (v) \) was subtracted from the reaction endothermicity. That is, \( k_v (T) \propto \exp \left( -\frac{\Delta E - E_v}{k_B T} \right) \). However, the reactivity of reaction (1) for \( H_2 (v \geq 1) \) is a very selective process, and the above assumption is often not realistic and can lead to uncertain predictions. Hence, an accurate estimation of hydride abundances requires one to compute the \( H_2 (v) \) level populations and to implement \( v \)-state-specific rate coefficients in chemical networks (Agúndez et al. 2010). This also applies to the chemistry of irradiated protoplanetary disks (e.g., Fedele et al. 2013; Raoua 2021).

When laboratory measurements are not possible, state-specific reaction rate coefficients, \( k_v (T) \), can be determined through ab initio calculations of the potential energy surface (PES) followed by a study of the reaction dynamics. Detailed calculations of state-specific rates of reaction (1) exist for \( X = C^+ \) (Zanchet et al. 2013b), \( X = S^+ \) (Zanchet et al. 2013a, 2019a), \( X = N^+ \) (Gómez-Carrasco et al. 2014), \( X = N^+ \) (Grozdanov et al. 2016; Gómez-Carrasco et al. 2022), \( X = S \) and \( SH^+ \) (Goicoechea et al. 2021), and \( X = O \) (Veselina et al. 2021). The above calculations contributed to explain the observed abundances of hydride molecules in interstellar and circumstellar environments. Furthermore, the formation of very reactive hydrides (most notably \( CH^+ \)) from hydrogen abstraction reactions involving vibrationally excited \( H_2 \) also determines much of the hydride excitation (Godard & Cernicharo 2013; Faure et al. 2017) and explains the observed extended \( CH^+ \) emission from FUV-irradiated molecular cloud surfaces (Morris et al. 2016; Goicoechea et al. 2019).

Here we study the state-specific behavior of reaction

\[
N(\text{S}) + H_2 (\Sigma_g^+, v = 0 \rightarrow 12) \rightarrow NH (\Sigma_u^+) + H, \tag{2}
\]

through dynamical (quantum and quasi-classical) calculations. Based on PDR model predictions using our new rate coefficients, we also searched for NH emission lines toward the Orion Bar and the Horsehead PDRs.

The paper is organized as follows. In Sect. 2 we briefly discuss the most salient differences of reaction (1) when \( X = C \), \( N \), O, and S are neutral or ionized. In Sect. 3, we focus on reaction (2) and summarize the details of our dynamical calculations to determine the state-specific reactive rate coefficients. In Sect. 4, we investigate their impact on PDR models adapted to the physical and illumination conditions in the two prototypical PDRs. Finally, in Sect. 5 we study the excitation of NH rotational lines, search for NH emission lines in submillimeter observations, and present a 3\( \sigma \) detection toward the Orion Bar PDR.

2. Reactivity of \( H_2 (v \geq 1) \) with abundant elements

The formation rate of hydride \( XH \) through reaction (1) depends on the abundance of element \( X \), the population of \( H_2 \) in different vibrational levels, and the particular characteristics and dynamics of reaction (1). Figure 1 shows the minimum energy paths for reactions of \( H_2 \) with \( X \). To make these plots, we took the analytical PESs from different studies: \( S(^3P) + H_2 \) from Maiti et al. (2004); \( S^+(^3S) + H_2 \) from Zanchet et al. (2019a);...
O(3P) + H₂ from Zanchet et al. (2019b); O*(5S) + H₂ from Martínez et al. (2004); N*(5) + H₂ from Poveda & Varandas (2005); N*(3P) + H₂ from Nyman & Wilhelmsson (1992); C*(3P) + H₂ from Harding et al. (1993); and C*(2P) + H₂ from Stoecklin & Halvick (2005).

In general, the endoergicity of reaction (1) depends on the relative stability of the species XH with respect to H₂ (i.e., their dissociation energy). Reactions involving cations X+ present a diverse behavior: exothermic for O+, endothermic for C+ and S+, and nearly thermoneutral for N+ (although Zymak et al. 2013 report a low endothermicity of 17 meV that is still under debate). Some of these reactions present a deep insertion well (C+ and N+) and others present a shallow well (O+). However, none of them present an energy barrier, except for the one attributed to the endothermicity. The lack of energy barriers is ultimately attributed to the presence of dangling orbitals in the atomic cations. These orbitals allow for the formation of new chemical bonds before H₂ bond dissociation.

Reactions involving neutral atoms, however, display a different and more homogeneous behavior. For all cases where X is in the ground electronic state, which is by far the most common situation in molecular clouds, reaction (1) is endoergic and possesses an energy barrier due to the lack of free dangling orbitals of the reactant 1S and 3P neutral atoms. The absence of dangling orbitals requires, first, the fragmentation of the H₂ molecule and, second, the formation of the hydride bond. This gives rise to a reaction barrier.

The presence of a well and/or a barrier along the reaction path introduces an important difference in the reaction mechanisms and, hence, in the reaction rate coefficients. For example, the presence of deep wells between the reactants leads to the formation of long-lived molecular complexes (e.g., CH*) in which there is an important energy transfer among all internal degrees of freedom.

During the approach of the two reactants in a reaction with no wells, one can consider that there is no flow of energy, from vibrational or rotational, to the translation degrees of freedom. If there is no barrier, the reaction threshold opens as soon as the total energy is above the zero-point energy of the products, thus overcoming the endothermicity. However, the presence of a barrier possess constraints depending on how the energy is distributed among the degrees of freedom and on the particular location of the barrier. According to Polanyi’s rules for barriers at the entrance channel (early barrier), the translational energy between reactants must be above the height of the barrier to overpass it (Polanyi & Wong 1969; Mok & Polanyi 1969). However, when the barrier is located in the products channel (late barrier), then the vibrational energy has to be higher than the reaction path.

3. Ab initio study of reaction N(4S) + H₂(v) → NH + H

In this section, we describe our study of reaction (2) and we determine the state-specific rate coefficients up to v = 12. We also compare the rates of analogous reactions having a different heavy element atom as reactant.

Table 1. Parameters of our quantum calculations using MADWAVE3 in reactant Jacobi coordinates.

<table>
<thead>
<tr>
<th>r_min, r_max, Å</th>
<th>N_e</th>
<th>R_abs, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1, 24</td>
<td>320</td>
<td>11</td>
</tr>
<tr>
<td>0.001, 24</td>
<td>512</td>
<td>11</td>
</tr>
<tr>
<td>140, 0</td>
<td></td>
<td>10, 15</td>
</tr>
<tr>
<td>4, 0.4 eV</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes. r_min ≤ r ≤ r_max is the H₂ internuclear distance. R_min ≤ R ≤ R_max is the distance between the H₂ center-of-mass and the nitrogen atom, and 0 ≤ γ ≤ π/2 is the angle between r and R vectors. The initial wave packet is described in R by a Gaussian centered at R = R₀ at an translational energy of E = E₀, and width ΔE. The total reaction probability was obtained by analyzing the total flux at r = r_max.

3.1. Quantum and quasi-classical calculations

Following our previous studies, we used the quantum wave packet method implemented in the MADWAVE3 package (Roncero 2021; Gómez-Carrasco & Roncero 2006; Zanchet et al. 2009). We used reactant Jacobi coordinates and determined the state-to-state reaction probabilities for each calculated angular momentum (Gómez-Carrasco & Roncero 2006). Table 1 lists the parameters used in the calculations. We performed these calculations for total angular momentum (J) and parity (p) under the inversion of coordinates, extracting the total reaction probability, P(Jp)(E). The total integral cross section for reaction N + H₂(v, j = 0) → NH + H was then obtained from the following usual partial wave expression:

\[
\sigma_J(E) = \frac{\pi}{(2j+1)k_{ej}^2} \sum_{J,p} (2J + 1)P(Jp)(E),
\]

where j is the initial rotational state of H₂ (here we adopt j = 0), E is the translational energy, and k_{ej} = \sqrt{E\mu}/\gamma, and μ = m_N2m_H/(m_N + 2m_H) is the reduced mass of the N + H₂ system.

We calculated the reaction probabilities for J = 0, 10, ..., 80. We employed the J-shifting-interpolation and extrapolation method (Aslan et al. 2012) to obtain the reaction probabilities of the intermediate J values by evaluating the total integral reactive cross section using the partial wave expansion up to J = 80. Finally, we determined the state-specific reaction rate coefficients by numerical integration of the cross section with

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a Boltzmann distribution for the translational energy (Zanchet et al. 2013b; Gómez-Carrasco et al. 2014). That is to say, 

\[ k(T) = \left[ \frac{8}{\pi \mu (k_B T)^2} \right]^{1/2} Q_e(T) \int_0^\infty E \sigma_e(E) e^{-E/k_B T} dE, \]  

(4)

where \( Q_e(T) \) is the electronic partition function.

For \( H_2 \) (\( \nu \geq 7 \)), we performed quasi-classical calculations using the MDwQT code (Sanz-Sanz et al. 2015; Zanchet et al. 2016; Ocaña et al. 2017). We sampled the initial conditions with the usual Monte Carlo method (Karplus et al. 1965). For each vibrational state of \( H_2 \), the initial internuclear distance and velocity distributions were obtained with the adiabatic switching method (Grozdanov & Solov’ev 1982; Qu & Bowman 2016; Nagy & Lendvay 2017). The initial rotational state of \( H_2 \) was set to zero. The distance between N and \( H_2 \) center of mass was initially set to 50 bohr, and we stopped the trajectories when the internuclear distance was longer than 60 bohr. The initial impact parameter was sampled between 0 and 15 bohr, according to a quadratic distribution. For each translational temperature, we ran between \( 2 \times 10^3 \) and \( 10^4 \) trajectories for each \( v \) and \( T \). The lower temperatures (\( T \approx 100 \) K) and vibrational states \( v = 7 \) and 8 require the largest number of trajectories. We determined the QCT state-specific rate coefficients as follows:

\[ k_e(T) = \sqrt{\frac{8 k_B T}{\pi \mu}} b_{\text{max}}^2 P_e(T), \]  

(5)

where \( b_{\text{max}}(T) \) is the maximum impact parameter and \( P_e(T) \) is the reaction probability at a constant temperature.

### 3.2. State-specific reaction rates and discussion

Figure 2a shows the calculated state-specific reaction rates from \( v = 0 \) to 12. Continuous curves show the quantum calculations and dashed lines show the QCT calculations. We specifically compared the quantum (curves) and classical (red squares) rate coefficients for \( H_2(v = 7) \). They show very good agreement except at 100 K, at which the reaction probability is very low and thus the statistical error is large. This supports the validity of the QCT rates obtained for \( v > 7 \). The right panel of Fig. 2 shows the resulting thermal rate coefficient computed as the Boltzmann average of the individual state-specific coefficients:

\[ k_{\text{th}}(T) = \frac{\sum_{v=0}^{12} k_e(T) e^{-E_v/k_B T}}{\sum_{v=0}^{12} e^{-E_v/k_B T}}. \]  

(6)

Most astrochemical models use \( k_{\text{th}}(T) \). This is the rate coefficient commonly provided by theorists and experimentalists. At low temperatures (\( T \ll E_v(H_2)/k_B \)), in most interstellar applications, the thermal rate coefficient is roughly that of \( H_2 \) in the ground vibrational state: \( k_{\text{th}}(T) \approx k_{\text{th}}(T) \) (Agúndez et al. 2010). Figure 2b also shows the available experimental rate coefficient of reaction (2) in the temperature range \( T = 1950-2850 \) K (Davidson & Hanson 1990). For \( T > 2300 \) K, our calculated thermal rate coefficient lies within the relatively large experimental error of the laboratory measurement (red shaded area). For \( T < 2300 \) K, our calculated rate is slightly below the experimental error. We attribute these slight differences to the fact that we neglect the rotational levels in the Boltzmann average. Still, we are confident that the overall good agreement validates the results of our calculations.

Table 2 lists the obtained state-specific reaction rate coefficients fitted by the usual Arrhenius-like form \( k_e(T) = \alpha (T/300 \text{K})^\gamma \exp(-\gamma/T) \). We note that these rate coefficients increase with temperature and with the initial \( H_2 \) vibrational level \( v \). For \( H_2(v \geq 3) \), the reaction becomes exergonic, but the reaction rate still behaves as if it has an energy threshold due to the location of the energy barrier in the PES.

Figure 3 (second panel from the bottom) shows the PES of a collinear H-H-N configuration as a function of the Jacobi distances \( R \), the distance between the N and the \( H_2 \) center-of-mass (whose derivative is proportional to the initial translational
velocity), and also as a function of $r$, the H$_2$ internuclear distance, thus associated with the vibrational energy. In this plot, the top of the barrier is along the thick black arrow, which is a graphical approximation of the reactive coordinate at the saddle point.

This saddle point corresponds to a long $r$ distance, that is to say a late barrier. This means that in order to overcome the energy barrier, some vibrational energy needs to be given to the $r$ coordinate. The forth blue contour plot corresponds to the energy of H$_2(v=3)$ and it is open, thus connecting reactants and products. Interestingly, one would expect that for H$_2(v=3)$, the reaction becomes exoergic without any threshold. However, this is not the case because the direction of the reaction coordinate at the top of the barrier is only approximately parallel to the arrow (Fig. 3). With an arrow parallel to the $x$ axis, the slope to overpass the barrier would have been along the $r$ coordinate, and the reaction with H$_2(v=3)$ would be roughly exoergic. However, the arrow has a non-negligible contribution along the $R$ coordinate. Hence, some energy must be given to the system along this $R$ coordinate initially (i.e., translational energy) to overcome the barrier. This late energy barrier implies that the reaction rate coefficients are very small at low temperatures but increase with $T$ and with the vibrational state even for very high-$v$ H$_2$ levels.

**Comparison with analogous reactions.** Figure 3 summarizes the qualitatively similar PESs of reactions between neutral atomic N, S, C, and O and vibrationally excited H$_2$. These reactions show a similar behavior, all being endothermic with a late barrier and no well. The moderate increase in the state-specific rate coefficients $k_v(T)$ with $v$ and temperature is produced by the presence of these barriers. On the other hand, endothermic hydrogen abstraction reactions involving N$^+$, S$^+$, and C$^+$, thus lacking energy barriers, behave differently. For example, reaction S$^+$ + H$_2(v)$ → SH$^+$ + H (Fig. 1) becomes exoergic for $v \geq 2$ and its associated rate coefficients do not show any threshold for $v \geq 2$ (Zanchet et al. 2019a). That is, they do not vary with temperature much. Figure 4 explicitly compares the $v=0$, 2, and 4 state-specific rate coefficients of reactions between H$_2(v)$ and N(3$^3$S), S(3$^3$S), and O(3$^3$P) (the latter is from Veselinova et al. 2021). As expected, the rate coefficients of reaction S$^+$ + H$_2(v)$ for $v \geq 2$ are nearly independent of temperature. However, the rate coefficients of reaction O + H$_2(v)$ still increase with $T$. A relevant difference between hydrogen abstraction reactions with O and N is the lower height of the energy barrier for reaction O(3$^3$P) + H$_2(v)$. This translates into
higher rate coefficients for the lower-\(v\) \(H_2\) vibrational states, and thus a stronger dependence on the production of interstellar OH, compared to NH, with gas temperature (Veselina et al. 2021). As we demonstrate in the next section, the formation of abundant NH specifically requires FUV-pumped \(H_2\) and the subsequent population of highly excited \(v\) levels. These processes take place at the irradiated surface of PDRs where elements with IP > IP(H), such as O and N, are in predominantly neutral form. On the other hand, reactions of neutral atomic carbon and sulfur with vibrationally excited \(H_2\) are less important because neutral atomic C and S only become abundant deeper inside the PDR, where the FUV radiation field is more attenuated and the fraction of \(H_2\) in vibrationally excited states drastically decreases. For comparison purposes, in Appendix A we calculate QCT state-specific rate coefficients of the analogous reaction \(S^{(2)} + H_2(v=0–12) \rightarrow SH + H_2\) (see Table A.1). Despite the similar behavior of the rate coefficients of reactions \(N^{(2)} + H_2(v)\) and \(S^{(2)} + H_2(v)\), the impact of the latter ones on the formation of SH radicals is very small. The difference arises from the fact the \(S^+\) ions, and not S atoms, are the dominant sulfur reservoir in the PDR layers where vibrationally excited \(H_2\) is abundant (see Fig. A.2).

4. Effects of the state-specific rates on the NH abundance in FUV-irradiated gas

Dense PDRs contain enhanced densities of FUV-pumped \(H_2\). Infrared observations of the Orion Bar show the presence of \(H_2\) ro-vibrational emission lines from excited levels up to \(v = 12\) (e.g., Kaplan et al. 2021). The relative populations of these highly excited levels depart from thermal (purely collisional) excitation. Here we study the reactivity of highly vibrationally excited \(H_2\) with N atoms in illumination conditions appropriate to two iconic PDRs, the Orion Bar and the rim of the Horsehead nebula. Their impinging FUV radiation fields are

\[ N + H_2 \rightarrow NH + H \quad \text{(continuous curves, this work)} \]
\[ O + H_2 \rightarrow OH + H \quad \text{(dashed curves, Veselina et al. 2021)} \]
\[ S^+ + H_2 \rightarrow SH^+ + H \quad \text{(dotted curves, Zanchet et al. 2019a)} \]

\[ n_{\text{H}} = n(H) + 2n(H_2) \quad n_{\text{H}} = P_{\text{b}} / k_B T_k \]
\[ \zeta_{\text{CR}} = 10^{-16} \text{H}_2 \text{s}^{-1} \]
\[ RV = A\sqrt{E_B} \text{ cm} \text{s}^{-1} \]
\[ \text{Abundance O/H} = 3.2 \times 10^{-4} \]
\[ \text{Abundance C/H} = 1.4 \times 10^{-4} \]
\[ \text{Abundance N/H} = 7.5 \times 10^{-5} \]
\[ \text{Abundance S/H} = 1.4 \times 10^{-5} \]

**Table 3.** Main parameters used in the PDR models of the Orion Bar.

<table>
<thead>
<tr>
<th>Model parameter</th>
<th>Orion Bar</th>
<th>Horsehead</th>
</tr>
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<tbody>
<tr>
<td>FUV radiation field, (G_0)</td>
<td>(2 \times 10^4) Habing ((a))</td>
<td>100 Habing ((b))</td>
</tr>
<tr>
<td>Thermal pressure (P_{\text{b}} / k_B)</td>
<td>(2 \times 10^8) cm(^{-3})K ((c))</td>
<td>(4 \times 10^6) cm(^{-3})K ((d))</td>
</tr>
<tr>
<td>(n_{\text{H}} = n(H) + 2n(H_2))</td>
<td>(n_{\text{H}} = P_{\text{b}} / k_B T_k)</td>
<td></td>
</tr>
<tr>
<td>(\zeta_{\text{CR}} = 10^{-16} \text{H}_2 \text{s}^{-1})</td>
<td>(5.5) ((c))</td>
<td></td>
</tr>
<tr>
<td>(RV = A\sqrt{E_B} \text{ cm} \text{s}^{-1})</td>
<td>3.2 \times 10^{-4} ((f))</td>
<td></td>
</tr>
<tr>
<td>(\text{Abundance O/H})</td>
<td>1.4 \times 10^{-4} ((g))</td>
<td></td>
</tr>
<tr>
<td>(\text{Abundance N/H})</td>
<td>7.5 \times 10^{-5} ((h))</td>
<td></td>
</tr>
<tr>
<td>(\text{Abundance S/H})</td>
<td>1.4 \times 10^{-5} ((i))</td>
<td></td>
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</tbody>
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\(G_0 \approx 2 \times 10^4\) (Marconi et al. 1998) and \(G_0 \approx 100\) (Abergel et al. 2002), respectively.

To model the nitrogen chemistry in these two PDRs, we used the Meudon PDR code (Le Petit et al. 2006). We implemented the state-specific rates of reaction (2) calculated in Sect. 3 up to \(H_2(v = 12)\). In addition, we updated the rate coefficient of the destruction reaction \(NH + H \rightarrow N + H_2\) (relevant in PDRs due to the enhanced abundance of hydrogen atoms). We adopted the rate coefficient computed by Han et al. (2010), which is consistent with laboratory experiments of Adam et al. (2005). Our models also include specific reactions of \(o-H_2\) and \(p-H_2\) with \(N^+\) ions, for which we computed the \(H_2\) ortho-to-para (OTP) ratio at each cloud depth. We adopted the rate coefficients fitted from low-temperature ion trap experiments of Zymak et al. (2013). The reaction \(N^+ + H_2\) is thought to initiate the nitrogen chemistry in cold gas shielded from FUV radiation (e.g., Le Bourlot 1991; Dislaire et al. 2012). The PDR model performs a detailed treatment of the \(H_2\) FUV-pumping and vibrational excitation as well as of the penetration of FUV radiation into the cloud (Goicoechea & Le Bourlot 2007). Since we are mainly interested in the most irradiated outer layers of the PDR, where \(H_2\) molecules are effectively pumped by FUV photons, our models only include gas-phase chemistry (except for \(H_2\) formation; Bron et al. 2014). Following our previous studies, we use a constant thermal pressure \((P_{\text{b}} / k_B = n_{\text{H}} T)\). Table 3 summarizes

\(4\) The rate coefficient of reaction \(N^+({^3}P_j) + H_2(j) \rightarrow NH^+ + H\) depends on the \(H_2(j)\) rotational level population (i.e., on the OTP ratio). At low temperatures, reactions with \(o-H_2\) are faster (e.g., Marquette et al. 1988; Zymak et al. 2013), but \(p-H_2\) is also less abundant. In our models, we ignore the different reactivities of \(N^+\) in its three \(^3P_j\) fine structure levels (separated by \(\Delta E_{ij} / k_B = 70\) K and 188 K, respectively). Zymak et al. (2013) derived the rate coefficients considering that only the three lower spin-orbit states contribute to the reaction and that the highest excited \(N^+\) fine-structure state \({^3}P_2\) is not reactive (adiabatic behavior). Such an approximation changes the determination of the reaction rate coefficients for \(o-H_2\) and \(p-H_2\) especially at low temperatures. Recent quantum calculations including transitions among all spin-orbit states find that the reactivity of the state \({^3}P_2\) is not zero (Gómez-Carrasco et al. 2022). This implies a slight reduction in the rate coefficients for \(o-H_2\), especially at low temperatures. This agrees with new experimental results of Fanghaenel (2018), which take the contribution of the \({^3}P_2\) state into account.
**4.1. Strongly FUV-irradiated gas: The Orion Bar PDR case**

Figure 5 dissects the physical structure of the Orion Bar model as a function of cloud depth (along the illumination direction and in magnitudes of visual extinction, $A_V$). Figure 5a shows the decreasing gas temperature and increasing $H_2$ density gradient from the PDR edge to the more FUV-shielded cloud interior. It is important to note that $H_2$ molecules are efficiently photodissociated at the irradiated PDR surface ($A_V \lesssim 1$ mag). In these hot gas layers, the abundance of $H$ atoms is higher than that of $H_2$. However, a significant fraction of the existing $H_2$ is in highly excited vibrational states (shown in Fig. 5b). In particular, the fractional abundance of $H_2$ molecules in $v > 7$ states ($f_v$) with respect to those in the ground state $v = 0$ reaches $f_v \approx 3\%$. On the other hand, beyond $A_V \gtrsim 2$ mag, most hydrogen is in a molecular form, but $f_v$ becomes negligible and the fractional abundance of $H_2$ in vibrationally excited states ($n(H_2 v \geq 1) / n(H_2)$) sharply declines below $\lesssim 10^{-3}$. Therefore, we expect that any enhanced formation of $X$ hydrides through reactions of $X$ with highly vibrationally excited $H_2$ will take place in these $A_V < 2$ mag surface layers.

Figure 5c shows $k_v(T) \times f_v$, the contribution of each $H_2$ vibrational state to the $N + H_2(v) \rightarrow NH + H$ rate coefficient, as a function of cloud depth. Here $f_v(T)$ is the fractional population of vibrationally excited states ($v > 7$). To visualize the impact of the state-specific rate coefficients of reaction (2), Fig. 5d shows the predicted NH abundance peak, the amount of $H_2$ in vibrationally excited states sharply declines and both models predict the same NH abundance. The inclusion of state-specific rates for reaction (2) increases the total NH column density (integrated from $A_V = 0$ to 10 mag) by a factor of about $\sim 25$, from $N(NH) = 2.1 \times 10^{14}$ cm$^{-2}$ to $5.5 \times 10^{12}$ cm$^{-2}$. According to these models, most of the HN column density is located close to the PDR surface, between $A_V \approx 0.5$ and 2 mag.

Figure 6a shows the predicted $x(N)$, $x(N_2)$, $x(NH)$, $x(N^+)$, $x(NH^+)$, and $x(H_2 (v = 7))$ abundance profiles, and the fraction of $H_2$ in $v > 7$ states ($f_v$). Owing to the high ionization potential of neutral N atoms, $IP(N) > IP(H)$, neutral N atoms are the major nitrogen reservoir at the PDR surface and up to $A_V \approx 4$ mag. In the most irradiated PDR layers, even if the abundance of $H_2$ with respect to $H$ nuclei is still low, NH readily forms by reactions of $N$ with highly vibrationally excited $H_2$ (which is the main destruction pathway of $N$ in these layers). Destruction of $NH$ is initially driven by reactive collisions with abundant $H$ atoms ($NH + H \rightarrow NH_2 + H$). At the NH abundance peak, the density of $H$ atoms decreases (upper panel of Fig. 6a), but the FUV radiation field is still high. Hence, photodissociation dominates NH destruction. This happens because NH does not easily react with $H_2$. Indeed, reaction $NH + H_2 \rightarrow NH_2 + H$ is endothermic and possesses a high activation barrier, $E_a/k_B \approx 5700$ K (Linder et al. 1995). Although $NH_2$ is not detected in the Bar,
the role of the above reaction might be more relevant for FUV-pumped H$_2$. However, state-specific reaction rates have not been computed yet.

Beyond the NH abundance peak, at $A_V > 2$ mag, most H$_2$ is in the lowest-energy vibrational states and NH formation through reaction (2) becomes negligible (see the evolution of the total formation rate in Fig. 5d). At this point, other chemical reactions – notably those initiated by the hydrogen abstraction reactions N$^+ \rightarrow$NH$^+ \rightarrow$NH$^+_2 \rightarrow$NH$^+_3$ and finishing with the dissociative recombination of NH$_3^+$ and NH$_2^+$ ions – dominate the production of NH (e.g., Boger & Sternberg 2005; Dislaire et al. 2012). In the Orion Bar model, the number of N$^+$ ions is controlled by the photodissociation of N-bearing ions (such as NO$^+$ and NH$^+$) at the PDR edge, and by the cosmic-ray ionization rate at large cloud depths (through direct ionizations of N atoms and through reactions of N$_3$ with He$^+$). Figure 7 shows the contribution (in percent) of reactions N$^+$ + H$_2$(v) and N$^+$ + o/p-H$_2$ to the total formation rate of NH and NH$^+$, respectively. At the PDR edge, $A_V < 2$ mag, the production of NH is almost entirely dominated by reaction N$^+$ + H$_2$(v). The reaction N$^+$ + H$_2$ and NH photoionization contribute to the production of NH$^+$. However, due to the lower abundance of N$^+$ ions compared to that of neutral N atoms, the NH/NH$^+$ column density ratio is significantly above one. Deeper inside the cloud, as FUV radiation decreases, N$_2$ becomes the main nitrogen reservoir (at $A_V > 4$ mag in this model). Here, the nitrogen chemistry is initiated by reactions of N$^+$ with H$_2$, which is sensitive to the H$_2$ OTP ratio (red curve in Fig. 7). At larger $A_V$, grain chemistry associated with the formation and desorption of ammonia ice (Knacke et al. 1982; Wagenblast et al. 1993) may alter the dominant formation and destruction pathways of NH.

### 4.2. Mildly FUV-illuminated gas: The Horsehead PDR case

Figure 6b shows the abundance profiles predicted by our model of the Horsehead PDR (less intense FUV field and lower gas density). Only at the PDR surface ($A_V < 0.5$ mag) is the abundance of H$_2$ (with respect to H nuclei) in highly vibrationally excited states large enough, with $x$(H$_2$,v$\geq$7) $\approx 5 \times 10^{-10}$ at $A_V = 0.5$ mag (versus $\approx 3 \times 10^{-7}$ in the Bar). In addition, the fraction of H$_2$ in highly vibrationally excited levels is lower: $f_2 \approx 2 \times 10^{-6}$ at $A_V \approx 0.5$ mag versus $f_2 \approx 10^{-4}$ in the Orion Bar. The higher $x$(NH) abundance at the very surface of the Horsehead PDR compared to that in the Bar is a consequence of the lower density of H atoms and lower flux of FUV photons (i.e., lower NH destruction rate).

With respect to the nitrogen chemistry, the use of state-specific rates for reaction (2) does increase the production of NH by two orders of magnitude at the Horsehead surface. However, the enhancement factor quickly decreases deeper inside the PDR because the abundance of H$_2$(v$\gg$) diminishes with $A_V$ being steeper than in a strongly irradiated dense PDR, such as the Bar.
The total NH column density predicted by the Horsehead model, integrated from $A_V = 0$ to 10 mag, is $N(NH) = 1.2 \times 10^{12}$ cm$^{-2}$ (i.e., 4.5 times lower than in the Orion Bar). Compared to the Bar, the edge of Horsehead has lower abundances of N (i.e., 4.5 times lower than in the Orion Bar). Compared to the rate coefficients (computed by Toboła et al. (2011) up to level $N$), we simply scaled the available fine-structure-resolved NH–He collisions, we estimate the NH–H and integrated from spectral resolution submillimeter observations of the Orion Bar and Horsehead and search for NH emission lines.

5. Detectability of submillimeter NH emission lines

In this section, we study the excitation and detectability of NH rotational lines in dense PDRs. We also explore existing high-spectral resolution submillimeter observations of the Orion Bar and Horsehead and search for NH emission lines.

The electronic ground state of the NH radical is $^3\Sigma^−$. Hence, rotational levels with $N > 0$ show a triplet fine structure arrangement (for an energy diagram, see Klaus et al. 1997). In addition, the $I_H = 0.5$ and $I_N = 1$ nuclear spins lead to a hyperfine splitting of the fine structure levels. Being a light molecule, the lowest-energy rotational lines ($N = 1 − 0$) appear in the high-frequency submillimeter domain, at 946 GHz ($N_J = 1_0 − 0_1$), 974 GHz ($N_J = 1_1 − 0_0$), and 1000 GHz ($N_J = 1_1 − 0_1$). High resolution heterodyne observations allow one to detect and separately resolve some of these NH hyperfine structure (HFS) lines (Persson et al. 2010, 2012). Unfortunately, telluric absorption precludes the observation of these lines from ground-based telescopes.

5.1. Subthermal NH emission in PDRs

Inelastic collisions populate the rotationally excited molecular levels in dense molecular gas. However, NH is a hydride molecule with a large rotational constant and high spontaneous radiative decay rates, $A_J/N = 1 − 0 \approx 10^{−3}$ s$^{-1}$. This is about $10^5$ times larger than those of the widely observed CO $J = 1 − 0$ line. This means that the gas density at which the inelastic collision de-excitation rate coefficients ($\gamma_{i,j}$ in cm$^3$ s$^{-1}$) equal the spontaneous radiative emission rate – the so-called critical density $n_{cr}(N = 1 − 0) = 10^5$ cm$^{-3}$. This implies that even in dense molecular clouds ($n_H > 10^4$ cm$^{-3}$), NH rotational lines will be weakly (subthermally) excited. In other words, $n_{cr} \ll n_H$ results in $T_{rot} \ll T_K$. Together with the intricate NH HFS spectrum (the rotational partition function of NH at 150 K is $t_{CH}^3$), this means that, unless exceptionally abundant, interstellar NH emission lines will be faint.

Figure 8 shows the rotational temperature of the NH $N_J = 1_0 − 0_1$ fine-structure line (974 GHz) as a function of gas temperature for different $H_2$ densities. These curves are “single-slab” model results obtained from detailed nonlocal thermodynamic equilibrium (LTE) excitation calculations using a Monte Carlo code (Goicoechea et al. 2022, and references therein). They refer to optically thin NH line emission. The inspection of Fig. 8 shows that one can expect

6 To estimate the NH–H$_2$ and NH–H inelastic collision rate coefficients, we simply scaled the available fine-structure-resolved NH–He rate coefficients (computed by Tobola et al. (2011) up to level $N = 8$ and $T_K = 350$ K) by the square root of the reduced mass ratio. We also extrapolated them to higher temperatures.

The NH $N_J = 1_0 − 0_1$ line at 946 GHz appears in HIFI band 3b (observed in the Bar [ObsID 1342216830]), the NH $N_J = 1_1 − 0_1$ lines at 974 GHz appear in HIFI band 4a (observed in the Bar [ObsID 1342218628] and in the Horsehead PDR [ObsID 1342218215]). The NH $N_J = 1_1 − 0_1$ lines at 1000 GHz appear in HIFI band 6a (observed in the Orion Bar [ObsID 1342216828]).

7 We took the hyperfine levels and spectroscopic information tabulated in the Cologne Database for Molecular Spectroscopy (CDMS; Endres et al. 2016). These data contain various experimental spectra (Klaus et al. 1997; Flores-Mijangos et al. 2004; Lewen et al. 2004).

Fig. 8. Rotational temperature of the NH $N_J = 1_0 − 0_1$ fine-structure transition versus gas kinetic temperature, for different gas densities, obtained from non-LTE excitation and optically thin emission models.

5.2. 3σ detection of NH in the Orion Bar PDR

The Orion Bar and Horsehead were observed at the frequencies of NH ($N = 1 − 0$) lines with the HIFI receiver (de Graauw et al. 2010) on board Herschel. These observations are part of the HEXOS (PI: E. A. Bergin) and WADI (PI: V. Ossenkopf) guaranteed time key programs. The Orion Bar data belong to a fully calibrated line survey (Nagy et al. 2017). The Horsehead data belong to a deeper search of hydride molecules. These HIFI spectra around the NH ($N = 1 − 0$) lines have not been discussed in the literature. In principle, the spectral resolution (1.1 MHz or $<0.3$ km s$^{-1}$ at these frequencies) is high enough to resolve several HFS lines of the three fine structure transitions $N_J = 1_0 − 0_1$ (946 GHz), $N_J = 1_1 − 0_0$ (974 GHz), and $N_J = 1_1 − 0_1$ (1000 GHz). The Orion Bar: Fig. 9 shows HIFI observations of the Bar. The root mean square (rms) noise of these spectra is 80–90 mK per velocity channel. The 974 GHz spectra show an emission feature above the 3σ noise level that matches the velocity of the molecular emission in the Orion Bar ($v_{LSR} = 10.7$ km s$^{-1}$; e.g., Cuadrado et al. 2015) if the feature is at $\sim$974.479 GHz. This is exactly the frequency of the brightest line $F = 974.479$ MHz. This line is $\sim$974.479 GHz. This line is $\sim$974.479 MHz. This line is $\sim$974.479 MHz. This line is $\sim$974.479 MHz. This line is $\sim$974.479 MHz. This line is $\sim$974.479 MHz. This line is $\sim$974.479 MHz.
the nondetection of the fainter NH lines at \( \sim \) optically thin line emission. The model of the Bar is also consistent with the spectrum showing the relative strengths of the individual HFS components for the \( J = 1 \) lines HCN observed emission. However, the lower excitation and lower frequency of the PDRs. The green horizontal lines display the curves are single-slab models for the \( N = 11 \)–10 line cannot be responsible for this feature. Hence, the \( \sigma = 3 \) detection (at the line peak) at 974.479 GHz. The pink spectra in the upper panel of Fig. 9 shows the resulting synthetic NH spectra. Given the low signal-to-noise ratio \( (S/N) \) of the data, the model is also consistent with the nondetection of the fainter NH lines at \( \sim 946 \) and \( \sim 1000 \) GHz.

\( k_{\text{th}}(T) \) and \( k_{\text{nth}}(T) \). We reproduced the amplitude of the observed feature at 974 GHz with \( N(\text{NH}) = 1.3 \times 10^{13} \) cm\(^{-2} \). The red curve in Fig. 9 shows the \( \Delta v \) width and shape of the observed feature is a blend of several HFS lines (individually shown by the pink spectra in the 974 GHz panel of Fig. 9).

We modeled the NH HFS spectrum of the Orion Bar adopting \( T_{\text{rot}} = 13 \) K and a nonthermal gas velocity dispersion of \( \sigma_{\text{nth}} = 1 \) km s\(^{-1} \) \( (\Delta v_{\text{th}} = 2.355 \sigma_{\text{nth}}) \). We reproduced the \( \Delta v \) width and shape of the observed feature at 974 GHz with \( N(\text{NH}) = 1.3 \times 10^{13} \) cm\(^{-2} \). The red curve in Fig. 9 shows the \( \Delta v \) width and shape of the observed feature is a blend of several HFS lines (individually shown by the pink spectra in the 974 GHz panel of Fig. 9).

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For the Orion Bar, only the PDR model including state-specific reaction rate coefficients is consistent with the observed level of NH emission, especially if one considers that the PDR is below the sensitivity reached by Herschel observations. For the Orion Bar, only the PDR model including state-specific reaction rate coefficients is consistent with the observed level of NH emission, especially if one considers that the PDR is below the sensitivity reached by Herschel observations.

### Table 4. NH column density and line intensity predictions from multi-slab radiative transfer models (from \( A_V = 0 \) to 10 mag).

<table>
<thead>
<tr>
<th>Input</th>
<th>( N(\text{NH}) ) (cm(^{-2} ))</th>
<th>PDR model</th>
<th>Orion Bar</th>
<th>Horsehead</th>
</tr>
</thead>
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<tr>
<td>( k_{\text{th}}(T) )</td>
<td>( 2.1 \times 10^{11}(a) )–6.3 \times 10^{11}(b) )</td>
<td>( 7.1 \times 10^{11}(a) )</td>
<td>( 3 \sigma )</td>
<td></td>
</tr>
<tr>
<td>( k_{\text{nth}}(T) )</td>
<td>( 5.5 \times 10^{12}(a) )–1.6 \times 10^{13}(b) )</td>
<td>( 1.2 \times 10^{12}(a) )</td>
<td>( 3 \sigma )</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Input</th>
<th>( W(\text{NH at 974 GHz}) ) (mK km s(^{-1} ))</th>
<th>PDR model</th>
<th>Orion Bar</th>
<th>Horsehead</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{\text{th}}(T) )</td>
<td>( 5(a) )–15(b)</td>
<td>( 11(a) )</td>
<td>( 3 \sigma )</td>
<td></td>
</tr>
<tr>
<td>( k_{\text{nth}}(T) )</td>
<td>( 290(a) )–870(b)</td>
<td>( 17(a) )</td>
<td>( 3 \sigma )</td>
<td></td>
</tr>
<tr>
<td>Observations</td>
<td>( \sim 700 )</td>
<td>( &lt;25 )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Notes.** (a) For a face-on PDR. (b) Edge-on PDR with a tilt angle \( \alpha = 20^\circ \) (geometrical enhancement of a factor of three).

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8 We searched for other possible molecular carriers of this feature. The HCN \( J = 1 \)–0 transition is at 974.487 20 GHz (at only \( \sim 2.5 \) km s\(^{-1} \) of the observed emission). However, the lower excitation and lower frequency lines HCN \( J = 10 \)–9 and 9–8 are not detected (Nagy et al. 2017). Hence, the \( J = 11 \)–10 line cannot be responsible for this feature.

9 In terms of the integrated line intensity, the detection significance of the \( \sim 974.479 \) GHz feature over a 10 km s\(^{-1} \) wide window is \( \sim 5 \sigma \).
not completely edge-on and one allows for a small tilt angle of \(\alpha \leq 20^\circ\) with respect to a fully edge-on geometry (Jansen et al. 1995; Melnick et al. 2012; Andree-Labsch et al. 2017). This geometry implies that optically thin lines are limb-brightened, with an intensity enhancement of \(\text{sin}^{-1}\alpha\) with respect to a face-on PDR. The NH emission detected in the Bar is consistent with its formation by gas-phase reactions of N atoms with highly vibrationally excited \(\text{H}_2\) at the PDR surface and producing \(N(\text{NH}) \approx 10^{13} \text{cm}^{-2}\). Compared to other PDRs, the higher gas density in the Bar contributes to a more efficient collisional excitation of submillimeter NH rotational lines, thus leading to detectable emission lines. The nondetection of NH\(^+\), however, is consistent with the low column density predicted by PDR models, that is to say \(N(\text{NH}^+)\) of several \(10^{10} \text{cm}^{-2}\).

Our study implies that the detection of NH emission in PDRs traces strongly FUV-irradiated dense gas\(^{10}\). Protostellar cores such as OMC-2 FIR 4 (Kama et al. 2013), the Orion hot core (Crockette et al. 2014), or Orion South (Turner et al. 2016) do not show NH emission lines. Interestingly, bright NH submillimeter and far-IR lines have been reported in the circumstellar envelope around the eruptive massive binary system \(\eta\) Carinae (Morrison et al. 2020; Gull et al. 2020). This unusual nitrogen-rich gas environment \((N(\text{NH}) = 5 \times 10^{15} \text{cm}^{-2}; \text{Gull et al. 2020})\) is strongly illuminated by X-ray and FUV radiation emitted by the central massive hot evolved stars. We suspect that much of the NH formation in this complex environment is driven by reactions of overabundant N atoms with highly vibrationally excited \(\text{H}_2\).

### 7. Summary and conclusion

Hydrogen abstraction reactions \(X + \text{H}_2(v=0) \rightarrow \text{XH} + \text{H}\) involving neutral atoms such as O, C, S, and N are very endoergic and have substantial energy barriers. This implies that even their \(\text{H}_2(v \geq 1)\) vibrational state-dependent reaction rate coefficients rise with an increasing \(v\) level and gas temperature. Due to its high ionization potential, neutral N atoms constitute the initial reservoir of available gas-phase nitrogen in FUV-illuminated environments. We calculated the state-specific rate coefficients of reaction \(N^+(S^1) + \text{H}_2(v) \rightarrow \text{NH} + \text{H}_2\) in vibrationally excited levels up to \(v = 12\). The newly computed rate coefficients imply that reactions of N atoms with highly vibrationally excited \(\text{H}_2\) molecules (after FUV-pumping) enhance the formation of NH in strongly irradiated dense PDRs. For the Orion Bar conditions, we find a total NH column density of a factor \(\sim 25\) with respect to models that use the thermal rate coefficient. We predict that most of the NH column density in the Orion Bar arises from the PDR surface, between \(A_V \approx 0.5\) and 2 mag, where reactions of N atoms and \(\text{H}_2\) molecules at \(v = 0\) vibrational levels dominate the formation of NH radicals. Prompted by this result we searched for NH emission lines in the Herschel/HIFI spectra of the Orion Bar and Horsehead PDRs. Only toward the Bar we do report a 3\(\sigma\) emission feature at the \(\sim 974.479\) GHz frequency of the NH \(N_J = 1_2 - 0_1\) line. This emission level implies a NH column density of about \(10^{13} \text{cm}^{-2}\), which can only be matched by PDR models using the newly computed state-specific rate coefficients.

Owing to very subthermal excitation and endoergic formation, the rare detection of submillimeter NH emission lines seems associated with strongly FUV-irradiated dense gas. In addition to the Orion Bar, another likely candidate is the circumstellar environment around \(\eta\) Carinae, where particularly bright NH emission lines have been detected (Morrison et al. 2020; Gull et al. 2020). JWST will soon detect the infrared \(\text{H}_2\) emission from highly vibrationally excited levels in many FUV-irradiated environments. This will be a unique opportunity to quantify their populations and role in interstellar and circumstellar chemistry.

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10 Submillimeter NH lines are also detected in absorption toward the dust continuum emitted by massive (Fuente et al. 2010; Bruderer et al. 2010; Benz et al. 2010) and low-mass (Hily-Blant et al. 2010; Bachmann et al. 2010) star-forming cores. These detections refer to lower density \((n_\text{H}\lesssim 10^3 \text{cm}^{-3})\) and cold \((T_\text{K} = 10-20\) K) envelopes of gas shielded from strong FUV fields (i.e., negligible abundances of vibrationally excited \(\text{H}_2\)) and the nitrogen chemistry is initiated by reaction \(N^+ + \text{o}/p-\text{H}_2\) (e.g., Dislaire et al. 2012; Le Gal et al. 2014).
Appendix A: State-specific rates of reaction

$S(^3P) + H_2(^3Σ_g^+,v) → SH(X^3Π,λ) + H$

To further support the similar behavior of reaction (1) when $X$ is a neutral atom, we also studied the analogous reaction of $H_2(\nu)$ molecules with $S(^3P)$ atoms. This reaction also presents a late barrier (see Fig. 3). Goicoechea et al. (2021) previously reported quantum wave packet calculations of the reaction rate coefficients for $v=2$ and $v=3$. For $v=3$, the reaction becomes exoergic, and the initial vibrational energy of $H_2$ is higher than the energy barrier (see Fig. 1). Here we extend the calculations to higher $v$ values using QCT calculations similar to those described in Sect. 3.1.

Appendix A.1: QCT reaction rate coefficients up to $v=12$

We considered $S$ atoms in $^3P_J$ levels, with nine spin-orbit states, with energies 0, 396.640, and 573.64 cm$^{-1}$ for $J=2$, 1, and 0, respectively. We introduced the spin-orbit splitting a posteriori.

First, we calculated the rate coefficients for each vibrational state of $H_2(\nu)$ for each adiabatic electronic state of the $H_2+S(^3P)$ system, neglecting spin-orbit coupling. The three adiabatic states correlate to $S(^3P_A)$, with $\Lambda=0$, $\pm 1$ being the projection of the atomic electronic angular momentum. The $SH(X^3Π)$ state correlates with $S(^3P_{λ=1})$, which are degenerate at the collinear geometries considered in Figs. 1 and 3. The $S(^3P_{λ=0})$ state correlates with the $SH(A^3Σ^+)$ state, which is at 3.85 eV above $SH(X^3Π)$, and therefore its contribution to the reactivity is negligible at the energies considered here.

The two ground adiabatic states of the $SH$ system describing the $S(^3P) + H_2(^3Σ_g^+) → SH(X^3Π,λ) + H$ reaction are the $1^3A'$ and $1^3A''$ states, and here we consider the three-dimensional potential energy surfaces of Maiti et al. (2004). We performed quasi-classical trajectory calculations for each of these two adiabatic electronic states, and for $H_2(\nu=0.1, \ldots, 12)$. For each electronic vibrational states and each temperature, we calculated about $10^5$ trajectories. The two electronic states present very similar rate coefficients, and the rates of the two electronic $3^3A'$ and $3^3A''$ states were averaged for simplification purposes, that is, $K_i(T) = [K_{iA'}(T) + K_{iA''}(T)]/2$.

Second, considering that these two triply degenerate states correspond to $S(^3P_{J=2})$ (five states) and to one $S(^3P_{J=1})$ (one state) adiabatically, the total rate constant is then given by

$$k_i(T) = \frac{5 + e^{-396.64/K_iT}}{5 + 3e^{-396.64/K_iT} + e^{-573.64/K_iT}} K_i(T). \quad (A.1)$$

The obtained rate coefficients are shown in Fig. A.1, and the Arrhenius parameters used to fit them are listed in Table A.1 (including our determination of the thermal rate coefficient). They show a very similar behavior to that of reaction $N(^4S) + H_2(\nu)$ discussed in the main text. In particular, the rate coefficients show a threshold even for $v=3$, for which the reaction is exoergic and the vibrational energy is above the reaction barrier. This implies rate coefficients that have a positive dependence with temperature, even for vibrational excited $H_2$ levels. On the other hand, the analogous hydrogen abstraction reaction with $S^+$ ions, reaction $S^+(^4S) + H_2(\nu) → SH^+ + H_2$, shows the typical behavior of an exothermic reaction for $v \geq 2$, in other words a rate coefficient that is nearly independent of temperature (see Fig. 4).
Appendix A.2: Impact on the SH abundance in the Orion Bar

Figure A.2 shows the impact of the state-specific rate coefficients of reaction S($^3P$) + H$_2$(v) → SH + H, computed here up to v = 12, in a PDR model of the Orion Bar. The pink continuous curve shows the SH abundance profile using these rate coefficients. The pink dashed curve is for a model that uses the thermal rate coefficient. Despite these state-specific rate coefficients showing the same fundamental behavior as those of reaction N($^4S$) + H$_2$(v) → NH + H, the impact on the formation of SH radicals is very minor (an increase of \(~1\%\) in column density). This difference arises from the fact that S$^+$ ions, and not S atoms, are the dominant gas-phase sulfur reservoir in the PDR surface layers where highly vibrationally excited H$_2$ exist.

Goicoechea et al. (2021) present a detailed study of the chemistry of sulfur bearing hydrides in the Orion Bar. The SH abundance profile shown in Fig. A.2 is very similar to their Fig. 12 (implementing quantum rate coefficients up to $v = 3$ for reaction S($^3P$) + H$_2$(v) → SH + H).

Fig. A.2. Isobaric PDR model of the Orion Bar ($G_0 \approx 2 \times 10^4$, $P_{th}/k_B \approx 2 \times 10^8$ cm$^{-3}$ K) showing abundance profiles with respect to H nuclei. The gray dotted curve shows $f_7$, the fraction of H$_2$(v > 7) with respect to the ground (right axis gray scale). Solid curves refer to a model using state-specific reaction rates for reaction S($^3P$) + H$_2$(v) → SH + H, whereas dashed curves refer to a model using the thermal rate.