THE CHEMISTRY OF VIBRATIONALLY EXCITED H$_2$ IN THE INTERSTELLAR MEDIUM

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Abstract

The internal energy available in vibrationally excited H$_2$ molecules can be used to overcome or diminish the activation barrier of various chemical reactions of interest for molecular astrophysics. In this paper, we investigate in detail the impact on the chemical composition of interstellar clouds of the reactions of vibrationally excited H$_2$ with C$^+$, He$^+$, O, OH, and CN, based on the available chemical kinetics data. It is found that the reaction of H$_2$ ($v > 0$) and C$^+$ has a profound impact on the abundances of some molecules, especially CH$^+$, which is a direct product and is readily formed in astronomical regions with fractional abundances of vibrationally excited H$_2$, relative to the ground state H$_2$, in excess of $\sim 10^{-6}$, independently of whether the gas is hot or not. The effects of these reactions on the chemical composition of the diffuse clouds ζ Oph and HD 34078, the dense photon-dominated region (PDR) Orion Bar, the planetary nebula NGC 7027, and the circumstellar disk around the B9 star HD 176386 are investigated through PDR models. We find that formation of CH$^+$ is especially favored in dense and highly FUV illuminated regions such as the Orion Bar and the planetary nebula NGC 7027, where column densities in excess of $10^{13}$ cm$^{-2}$ are predicted. In diffuse clouds, however, this mechanism is found to be not efficient enough to form CH$^+$ with a column density close to the values derived from astronomical observations.

Key words: astrochemistry – ISM: molecules – molecular processes – photon-dominated region (PDR)

1. INTRODUCTION

As concerns the chemical modeling of interstellar clouds, state-to-state chemistry, i.e., that, which considers the quantum states of reactants and/or products in a given chemical reaction, has been traditionally ignored, mainly because the required chemical kinetics data are generally not available and because it is expected that it would not affect in a drastic way the predicted chemical abundances. Some attention however has been given to the different reactivity of ortho and para states of molecular hydrogen and its effect on various aspects of interstellar chemistry such as the formation of ammonia or the ortho-to-para ratio of c-C$_3$H$_2$ in cold dense clouds (Le Bourlot 1991; Park et al. 2006). The enhancement in the reactivity of molecular hydrogen when it is in a vibrationally excited state has also been considered in the past, mainly in the context of trying to explain the long standing problem of CH$^+$ formation in diffuse clouds (Stecher & Williams 1972; Freeman & Williams 1982; Garrod et al. 2003), but also in the study of the chemistry of dense photon-dominated regions (PDRs; Tielens & Hollenbach 1985; Sternberg & Dalgarno 1995) and shocked regions (Wagner & Graff 1987; Hollenbach & McKee 1989). These studies assumed different reactivity enhancements for reactions of vibrationally excited H$_2$ with species such as C$^+$, O, or C, and found that whereas in the case of diffuse clouds a too large fraction of H$_2$ $v > 0$ is required to explain the formation of CH$^+$ with the observed abundance, in the case of dense PDRs there are important effects for the chemistry.

In this paper, we look again at the chemistry of vibrationally excited H$_2$ in the light of some experimental and theoretical studies carried out in the last years, which have been essentially ignored by the astrochemical community, and investigate the implications for various astronomical regions where a relatively large fraction of vibrationally excited H$_2$ has been observed or is expected to be present.

2. THE CHEMISTRY OF VIBRATIONALLY EXCITED H$_2$ 2.1. Basics

The main feature that characterizes the chemistry of H$_2$ in excited vibrational states—as compared to that of H$_2$ in the ground vibrational state—is that the internal energy of the excited hydrogen molecule can be used to overcome or diminish activation barriers which are present when H$_2$ is in its ground vibrational state. Several experimental and theoretical studies have demonstrated that such behavior occurs for some reactions of H$_2$ which are of relevance for astrophysics, the kinetic data of which are detailed in Table 1 and Figure 1.

The first reaction that draws our attention is

\[
\text{H}_2 + \text{C}^+ \rightarrow \text{CH}^+ + \text{H} \quad (1)
\]

which is well known to possess an endothermicity of 0.37 eV ($\sim$4300 K). It has long been thought that such endothermicity could be overcome by vibrationally excited H$_2$ (the $v = 1$ levels have energies $>0.5$ eV above the ground state), a hypothesis that gained experimental support with the study of Jones et al. (1986) and the more recent measurements of Hierl et al. (1997). These latter authors were able to measure the rate constant of H$_2$($v = 1$) + C$^+$ over the 800–1300 K temperature range and found it to be in the range $1–2 \times 10^{-9}$ cm$^3$ s$^{-1}$, i.e., essentially

4 In regard to the chemistry of vibrationally excited H$_2$, it is worthwhile to comment on the difference between a state-specific and a thermal rate constant. The thermal rate constant, usually provided by experimental and theoretical chemists and used in interstellar chemical models, is the thermal average of the individual state-specific values, i.e., the sum over all H$_2$ states of the state-specific rate constant multiplied by the thermal fractional population of that H$_2$ state. It turns out that since the vibrationally excited levels of H$_2$ are very high in energy and thus poorly populated in thermal conditions, except at high temperatures ($>1000$ K), we expect the thermal rate constant to be essentially equal to the state-specific H$_2$ $v = 0$ rate constant, so that hereafter we use both terms interchangeably.
equal to the Langevin collision rate \((1.6 \times 10^{-9} \text{ cm}^3 \text{s}^{-1})\), and to show a slight negative temperature dependence. This is the typical behavior of exothermic ion-non-polar neutral reactions which have a temperature-independent rate constant close to the collision limit, and indicates that it is quite safe to adopt also the collision rate at low temperatures for the reaction of \(H_2(v = 3) + O + OH\). In connection with this we note that rate coefficients for reaction (1) have been computed by Gerlich et al. (1987) for selected initial rotational levels \((j = 0, 7)\) of \(H_2\) in the ground vibrational state. This work was combined with guided-beam measurements and a good agreement between the experimental results and the statistical calculations was observed. Gerlich et al. (1987) found that the state-specific rate constants may be well approximated by Arrhenius expressions (see Table 1 and Figure 1) in which as \(j\) increases the exponential factor decreases by an amount equal to the energy of the \(j\) level. All this indicates that the energy of excited \(H_2\) in reaction (1) is effectively used to diminish or overcome the endothermicity of the reaction, and that for \(H_2\) states with \(v > 0\) the reaction proceeds at the collision rate.

The second reaction on which we focus is

\[
H_2 + H^+ \rightarrow He + H + H^+ \tag{2}
\]

which is strongly exothermic but shows an extremely small rate constant, some \(10^{-14} \text{ cm}^3 \text{s}^{-1}\) below 300 K (Schauer et al. 1989), which indicates the presence of an important activation barrier. Jones et al. (1986) have studied the kinetics of this reaction experimentally at room temperature and found that when \(H_2\) is in a vibrational state \(v > 1\) the reaction proceeds at about the collision limit, \(1.8 \times 10^{-9} \text{ cm}^3 \text{s}^{-1}\), a value that we adopt hereafter.

Another interesting reaction is

\[
H_2 + O \rightarrow OH + H \tag{3}
\]

Table 1

| No. | Reaction | \(k \text{ (cm}^3 \text{s}^{-1})\) | \(\Delta T \text{ (K)}\) | \(\Delta H_0(0 \text{K}) \text{(K)}\) | Reference |
|-----|----------|-----------------|-----------------|-------------------|----------|
| 1   | \(H_2 + C^+ \rightarrow CH^+ + H\) | \(7.0 \times 10^{-12} \exp(-4537/T)\) | 400–1300 | \(+4280\) | (1) |
| 2   | \(H_2(v = 1) + C^+ \rightarrow CH^+ + H\) | \(1.58 \times 10^{-10} \exp((-4827 - E_j/k)/T)\) | 200–1000 | \(+4280, -310\) | (2) |
| 3   | \(H_2(v > 1) + He^+ \rightarrow He + H + H^+\) | \(3.7 \times 10^{-14} \exp(-35/T)\) | 10–300 | \(-75560\) | (3) |
| 4   | \(H_2 + OH \rightarrow H_2O + H\) | \(3.52 \times 10^{-13} \exp(-3241/T)\) | 297–3532 | \(+920\) | (5) |
| 5   | \(H_2(v = 0) + O \rightarrow OH + H\) | \(1.68 \times 10^{-10} \exp(943/T)\) | 100–500 | \(-5070\) | (6) |
| 6   | \(H_2(v = 2) + O \rightarrow OH + H\) | \(1.52 \times 10^{-10} \exp(209/T)\) | 100–500 | \(-10720\) | (6) |
| 7   | \(H_2(v = 3) + O \rightarrow OH + H\) | \(2.07 \times 10^{-11} \exp(-412/T)\) | 100–4000 | \(-16040\) | (6) |
| 8   | \(H_2 + OH \rightarrow H_2O + H\) | \(2.22 \times 10^{-12} \exp(-1751/T)\) | 200–3000 | \(-7370\) | (5) |
| 9   | \(H_2(v = 1) + OH \rightarrow H_2O + H\) | \(1.52 \times 10^{-11} \exp(-902/T)\) | 250–2000 | \(-13360\) | (7) |
| 10  | \(H_2(v = 1) + CN \rightarrow HCN + H\) | \(1.17 \times 10^{-12} \exp(-1188/T)\) | 200–3500 | \(-10250\) | (5) |
| 11  | \(H_2 + CN \rightarrow HCN + H\) | \(9.65 \times 10^{-12} \exp(-1397/T)\) | 200–1000 | \(-16240\) | (8) |

Notes. When no specific state of \(H_2\) is indicated the expression for \(k\) corresponds to the thermal rate constant. The reaction enthalpies \(\Delta H_0(0 \text{K})\) have been computed from the formation enthalpies at 0 K of each species, taken from NIST-JANAF Thermochemical Tables (Chase 1998), while for the \(H_2\) state-specific reactions the level energies of \(H_2\) have been taken from Dabrowski (1984).

\(\Delta T\) is the temperature range over which the rate constant has been studied.

\(E_j\) is the energy of each rotational level of \(H_2\) \((v = 0, j)\) relative to the ground state \(v = 0, j = 0\) \((E_1 = 170.5 \text{ K}, E_2 = 509.9 \text{ K}, E_3 = 1015.2 \text{ K}, E_4 = 1681.7 \text{ K}, E_5 = 2503.9 \text{ K}, E_6 = 3474.4 \text{ K}, \text{ and } E_7 = 4586.4 \text{ K}; \text{ Dabrowski 1984})\).

\(\Delta H_0(0 \text{K})\) is the energy of each rotational level of \(H_2\) \((v = 0, j)\) relative to the ground state \(v = 0, j = 0\).

Ref. (1) Hiesel et al. 1997; (2) based on Gerlich et al. 1987; (3) UMIST Database for Astrochemistry (Woodall et al. 2007); (4) Jones et al. 1986; (5) NIST Chemical Kinetics Database (http://kinetics.nist.gov/kinetics/); (6) Sultanov & Balakrishnan 2005; (7) Zeller & Steinert 1981; (8) Tuong 1995; (8) Zeller et al. 1998.

which is known to be endothermic by 0.08 eV \((\sim 900 \text{ K})\) and to possess an even higher activation barrier of about 0.4 eV \((\sim 4800 \text{ K})\). Recently Sultanov & Balakrishnan (2005) have calculated the rate constants for reaction (3) with \(H_2\) in various vibrational states \((v = 0–3)\) and have found that although the rate constant is noticeably enhanced as the vibrational state of \(H_2\) is increased, the reaction does not proceed at the collision rate limit for \(H_2(v = 0)\) but an activation barrier persists even when \(H_2\) is in the \(v = 3\) state (see Figure 1).

The exothermic reaction

\[
H_2 + OH \rightarrow H_2O + H \tag{4}
\]

possesses an activation barrier which can be partially overcome, when \(H_2\) is in the first excited vibrational state (Zeller & Steinert 1981; Tuong 1995, see Figure 1). Something similar occurs for the exothermic reaction

\[
H_2 + CN \rightarrow HCN + H \tag{5}
\]
Let us consider a region with a gas kinetic temperature $T$ where H$_2$ levels are not thermally populated, so that the fractional abundance of vibrationally excited H$_2$ is $f^* = n(H_2 v > 0)/n(H_2 v = 0)$, and the generic reactions

$$H_2(v = 0) + X \rightarrow \text{products},$$

so that $\Delta k(T) = k^*(T)/k^0(T)$ is the rate constant enhancement at a temperature $T$. For reaction (7) to become important it has to be competitive with respect to reaction (6), i.e., $f^* \Delta k(T) > 1$, and also with respect to other reactions which consume the reactant X. According to this, reactions such as H$_2$ + CN, which has a moderate rate enhancement ($\Delta k \lesssim 10$), need a very high abundance of vibrationally excited H$_2$ ($f^* > 10^{-10}$) to have some impact on the chemistry. On the other hand, reactions with a very high rate constant enhancement, such as that of H$_2$ + C$^+$ for which $\Delta k \sim 10^{10}$ at 200 K, just need a moderate abundance of vibrationally excited H$_2$ ($f^* > 10^{-10}$). This is however a condition necessary but not sufficient to have some impact on the chemistry as the reaction rate of, in this case, H$_2(v > 0)$ + C$^+$ needs also to be large enough compared to other reactions which consume C$^+$.

### 2.2. Implications for the Interstellar Medium

We may state that the importance of the chemistry of vibrationally excited H$_2$ is limited to reactions with a large rate constant enhancement and to astronomical regions with a high abundance of vibrationally excited H$_2$. In order to get a quantitative estimate of the impact of these reactions on the chemistry of the interstellar medium we have run single point time-dependent chemical models covering a wide range of the space of parameters: fraction of vibrationally excited H$_2$ ($f^*$), density of hydrogen nuclei ($n_H$), far-ultraviolet (FUV) radiation field strength ($j_x$, relative to the Draine interstellar radiation field; Draine 1978), and gas kinetic temperature ($T$).

We consider 127 different species composed of the elements H, He, C, N, O, and S, whose abundances are assumed to be solar (Asplund et al. 2009) with a 25% depletion for elements heavier than He, and assume that initially all the elements are in atomic form, either neutral or ionized. The chemical network comprises 2307 gas-phase reactions whose rate constants have been mostly taken from Agúndez & Cernicharo (2006) and from the UMIST database for astrochemistry (Woodall et al. 2007), some of them revised according to the most recent literature on chemical kinetics. The photodissociation rates of H$_2$ and CO have been taken from Lee et al. (1996). The adopted visual extinction is 0.5 mag and the cosmic-ray ionization rate per H$_2$ molecule is $5 \times 10^{-17}$ s$^{-1}$. We do not consider grain surface reactions except for the formation of H$_2$, which is assumed to occur with a rate constant of $3 \times 10^{-17}$ cm$^3$ s$^{-1}$, the canonical value in typical diffuse clouds (Jura 1975).

This quite standard chemical network is completed by adding the reactions of vibrationally excited H$_2$ detailed in Table 1. Thus, H$_2$ ($v = 1$) is included as a new chemical species with a fractional abundance $f^*$, relative to the ground state H$_2$, which is kept fixed at four different values (0, $10^{-6}$, $10^{-5}$, and $10^{-4}$), independently of the mechanism responsible of the excitation of H$_2$. The amount of H$_2$ ($v > 1$) is important for reactions (2) and (3) so that we also consider H$_2$ in the $v = 2$ and $v = 3$...
states with populations which are 1/3 and 1/9 respectively of that in the $\nu = 1$ state, values typically attained in interstellar clouds with an important fraction of vibrationally excited H$_2$ (e.g., van Dishoeck & Black 1986; Meyer et al. 2001). In these exploratory models, we do not distinguish between the different reactivity of H$_2$ in the various rotational levels of the ground vibrational state.

The abundances of various species are found to be sensitive to the fraction of vibrationally excited H$_2$. In Figure 2, we plot the steady-state abundance of some of these species for various fractional abundances of H$_2$ ($\nu = 1$) as a function of the $n_{HI}/\chi$ ratio. The steady-state abundances are found to depend on this latter ratio rather than on either $n_{HI}$ or $\chi$. For the results shown in Figure 2 a density of hydrogen nuclei of $10^3$ cm$^{-3}$ has been adopted, so that the FUV field strength has been varied. Reactions of vibrationally excited H$_2$ have a larger impact on the chemistry at low temperatures, since as discussed previously the rate constant enhancement $\Delta k$ of the various reactions is larger. The results shown in Figure 2 correspond to a relatively low temperature of 100 K.

The molecule whose abundance is more affected by the reactions of vibrationally excited H$_2$ is the methylidyne cation (CH$^+$), which for fractional abundances of H$_2(v=1)$ above $10^{-7}$--$10^{-6}$ is readily formed by the reaction between H$_2(v=1)$ and C$. The steady-state abundance of CH$^+$ approximately scales with the fraction of H$_2(v=1)$ and reaches its maximum abundance for $n_{HI}/\chi$ ratios in the range 1--100. By running models at different kinetic temperatures we find that above 400--500 K the reaction between H$_2(v=0)$ and C$^+$ starts to proceed and the abundance of CH$^+$ depends to a much lesser extent on the fraction of vibrationally excited H$_2$.

The abundances of CH$^+_2$ and CH$_3^+$ are strongly linked to that of CH$^+$ by the chain of exothermic reactions

$$\text{CH}^+ + \text{H}_2 \rightarrow \text{CH}_2^+ \rightarrow \text{CH}_3^+ \rightarrow$$

which stops at CH$_3^+$, as this species does not react fast with H$_2$. Therefore, in those conditions in which CH$^+$ reaches a relatively high abundance, CH$_2^+$ and CH$_3^+$ do so (see Figure 2). Some other species such as CH, OH, and H$_2$O also experience a moderate abundance enhancement when CH$^+$ is formed. The radical CH is formed by the dissociative recombination with electrons of the cations CH$_2^+$ and CH$_3^+$, while OH and H$_2$O are produced by a sequence of reactions that starts with the photodissociation of CH$^+$ and production of H$^+$ followed by

$$\text{O} + \text{H}^+ \rightarrow \text{OH}^+ \rightarrow \text{OH}^+ + \text{H}_2 \rightarrow \text{H}_2\text{O}^+ \rightarrow \text{OH}_2.$$  

The reaction of vibrationally excited H$_2$ and atomic oxygen has little effect on the abundance of OH for most of the conditions explored. It does contribute to OH formation just for fractional abundances of H$_2(v=1)$ in excess of $10^{-4}$ and for kinetic temperatures around 300 K. For much lower temperatures, activation barriers of the reactions H$_2(v>0) + \text{O}$ prevent reaching a high enough OH formation rate whereas for much higher temperatures the rate constant enhancements $\Delta k$ are low and OH is mostly formed by the reaction of H$_2(v=0) + \text{O}$. As concerns the reactions of vibrationally excited H$_2$ with He$^+$, OH, and CN, they have almost no impact on the chemistry as the rate constant enhancements are just moderate and require a very large fraction of vibrationally excited H$_2$ to compete with the corresponding reactions of H$_2(v=0)$.

In summary, from the five reactions of vibrationally excited H$_2$ considered here, only that with C$^+$ has a large impact on the abundances of some species, especially CH$^+$, in those astronomical regions which are not too warm (with kinetic temperatures below a few hundreds of degrees Kelvin) and which have a moderately high fraction of vibrationally excited H$_2$ (in excess of $10^{-7}$--$10^{-6}$). Reactions of H$_2(v>0)$ with He$^+$, O, OH, and CN are less likely to affect the chemistry of interstellar clouds unless large amounts of vibrationally excited H$_2$ are present.

3. EFFECTS ON SELECTED ASTRONOMICAL SOURCES

Vibrationally excited molecular hydrogen is commonly observed in PDRs, where the H$_2$ $v>0$ levels are excited by FUV fluorescence, and in shocked gas where the excitation is mainly collisional. Among these two types of regions the chemistry of vibrationally excited H$_2$ is expected to be less important in shocked regions since kinetic temperatures are usually very high and the H$_2$ level populations are not as far from thermalization.
as they are in PDRs (Burton 1992). Hereafter we thus focus on the case of PDRs to investigate the effects of the reactions of vibrationally excited H$_2$ onto the gas chemical composition.

For that purpose we have utilized an updated version of the Meudon PDR code,\textsuperscript{7} a photochemical model of a plane parallel and stationary PDR (Le Petit et al. 2006; Goicoechea & Le Bourlot 2007; González García et al. 2008), to compute the chemical and physical structure as a function of the cloud depth for various PDR-like regions. Penetration of FUV radiation strongly depends on dust grain properties through dust absorption and scattering of FUV photons which, in addition, determine the efficiency of the dominant heating mechanisms of the gas (photoelectric heating). In this work, we use standard dust properties, i.e., grain sizes follow a power-law distribution (Mathis et al. 1977; Goicoechea & Le Bourlot 2007) and explicitly determine the gas temperature gradient by solving the cloud thermal balance (see Le Petit et al. 2006). We have used the chemical network described in the previous section and the reactions of excited H$_2$ shown in Table 1. For the reaction between H$_2$ and C$^+$ we adopt the rotational state-specific rate constant expressions (2 in Table 1) for H$_2$ ($J \leq 7$) and assume the Langevin value (3 in Table 1) for H$_2$ ($J > 7$ or $v > 0$), states for which the reaction becomes exothermic. Under thermal conditions this approach results in a value equivalent to the thermal rate constant (1) in Table 1, at worst a factor of $\sim 2$ larger in the high temperature range ($>1000$ K), where the rate constant starts to be dominated by H$_2$ $v > 0$ states.

We consider (de-)excitation of H$_2$ levels by collisions with H$_2$, H, and He (Le Bourlot et al. 1999). Collisions with H$^+$ are also included based on the recent work of Huestis (2008), although they are found to be not important. Concerning collisions with electrons, the rates of vibrational de-excitation of H$_2$ $v = 1 \rightarrow 0$ are typically a few $10^{-10}$ cm$^3$ s$^{-1}$ (from the cross sections recommended by Yoon et al. 2008), which implies a critical density of electrons of $\sim 10^3$ cm$^{-3}$. In low density regions, such as diffuse clouds, the electron density is much lower and electron-impact vibrational excitation is negligible, although in denser regions with a high ionization degree, such as planetary nebulae, electrons could play a role in producing non-thermal H$_2$ vibrational populations. The implementation of (de-)excitation of H$_2$ by collisions with electrons is however not straightforward as only a few state-to-state cross sections are available (Yoon et al. 2008).

We are mainly interested in investigating how important is the effect of the chemistry of vibrationally excited H$_2$ in the various regions. We thus have systematically run for the different sources a model in which we adopt the thermal rate constant expressions for all reactions of H$_2$ (standard model) and another one including the state-specific rate constants for the reactions of excited H$_2$ detailed in Table 1 (H$_2^*$ model).

3.1. Diffuse Clouds: ζ Oph and HD 34078

We first focus on a well-known diffuse cloud such as ζ Oph, whose parameters (see Table 2) have been taken from van Dishoeck & Black (1986). In Figure 3, we show as a function of $A_V$ the abundance of some species while the calculated column densities are given in Table 2. The largest effects of the chemistry of vibrationally excited H$_2$ are seen at the edges of the cloud ($A_V < 0.1$) where there is an important fraction of H$_2$ ($v > 0$), which gives rise to an increase in the abundance of CH$^*$. Note that the sharp increase of $f^*$ (the ratio of vibrationally excited to ground state H$_2$) up to $\sim 10^{-3}$ at the very outer edges ($A_V < 0.001$) is produced by the decrease in the abundance of H$_2$ ($v = 0$), relative to total hydrogen, while that of H$_2$ ($v > 0$) keeps roughly constant. In this regime large $f^* \Delta k(T)$ ratios are attained (see discussion at the end of Section 2.1) and reactions of vibrationally excited H$_2$ increase their importance with respect to those of the ground state H$_2$, but not necessarily with respect to other processes (e.g., photodissociations). That is why the jump of $f^*$ at the outer edge of ζ Oph is not followed by the abundance of CH$^*$ (see Figure 3).

In any case, as the fraction of H$_2$ ($v > 0$) remains relatively low ($f^* < 10^{-7}$) throughout most of the cloud, the total column density of CH$^*$ is not dramatically affected. It increases by about a factor of 2 (see Table 2) but remains well below the observed value of $2.9 \times 10^{13}$ cm$^{-2}$ (see van Dishoeck & Black 1986). This relatively low fraction of vibrationally excited H$_2$ is in agreement with astronomical observations of ζ Oph (Federman et al. 1995), and implies that for quiescent diffuse clouds the chemistry of vibrationally excited H$_2$ does not have dramatic effects on the global chemical composition of the cloud.

Large fractions of vibrationally excited H$_2$ are not usually observed in diffuse clouds, except for a few lines of sight: HD 37903 (Meyer et al. 2001) and HD 34078 (Boissé et al. 2005, 2009), although its presence seems to be related to a dense component exposed to a high FUV field arising from nearby hot stars. In Figure 4, we show the results obtained for the dense component of HD 34078, called the “hot PDR” by Boissé et al. (2005), whose parameters have been taken from these authors (see Table 2). In this case, due to the large FUV field, a high fraction of H$_2$ ($v > 0$) is maintained throughout the cloud. Thus, the reaction between H$_2$ ($v > 0$) and C$^+$ readily occurs affecting the abundance of various species (see column densities in Table 2), most notably CH$^*$ whose abundance is increased by 2 orders of magnitude with respect to that obtained in the standard model, yet remaining below the observed value ($6.5 \times 10^{13}$ cm$^{-2}$; see Boissé et al. 2005). We note that the differences between the column densities calculated in our standard model and those obtained by Boissé et al. (2005) are most likely due to differences in the chemical network utilized. For instance, the larger column density of CH$^*$ obtained by them is to a large extent due to the larger rate constant they adopt for the radiative association between C$^+$ and H$_2$: $1.7 \times 10^{-15}$ cm$^3$ s$^{-1}$ (upper

\textsuperscript{7}See http://pdr.obspm.fr/PDRcode.html
### Table 2
Calculated Column Densities of Selected Species in the Studied Astronomical Sources

|       | ζ Oph | HD 34078 “hot PDR” | Orion Bar | NGC 7027 | HD 176386 |
|-------|-------|--------------------|-----------|-----------|-----------|
| $n_1$ (cm$^{-3}$) | 600   | $10^4$            | $10^5$    | $8 \times 10^6$ | $3 \times 10^7$ |
| $\chi$ | 4.4   | 10$^4$ | 10$^5$ | 3 \times 10$^5$ | 1.25 \times 10$^6$ |
| $A_{\text{int}}^{\text{total}}$ | 0.87  | 1.0   | 3 \times 10$^5$ | 2.5 | 0.9 |
| $T(K)$ | 40–50 | 200–300 | 20–700 | 200–800 | 95–120 |

|       | Standard $\rightarrow$ H$_2$ | Standard $\rightarrow$ H$_2$ | Standard $\rightarrow$ H$_2$ | Standard $\rightarrow$ H$_2$ | Standard $\rightarrow$ H$_2$ |
|-------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| H     | $1.2 \times 10^{20} \rightarrow \sim$ | $1.6 \times 10^{21} \rightarrow \sim$ | $1.4 \times 10^{21} \rightarrow \sim$ | $2.1 \times 10^{21} \rightarrow \sim$ | $1.1 \times 10^{20} \rightarrow \sim$ |
| H$_2$ | $7.6 \times 10^{20} \rightarrow \sim$ | $1.6 \times 10^{20} \rightarrow \sim$ | $7.7 \times 10^{20} \rightarrow \sim$ | $1.3 \times 10^{21} \rightarrow \sim$ | $8.8 \times 10^{20} \rightarrow 7.9 \times 10^{20}$ |
| H$_2$(v > 0) | $3.7 \times 10^{13} \sim$ | $4.2 \times 10^{15} \sim$ | $2.2 \times 10^{14} \sim$ | $4.9 \times 10^{17} \rightarrow 4.2 \times 10^{17}$ | $1.8 \times 10^{14} \rightarrow \sim$ |
| C$^+$ | $5.6 \times 10^{17} \sim$ | $2.5 \times 10^{17} \sim$ | $7.5 \times 10^{17} \sim$ | $4.6 \times 10^{17} \rightarrow 3.4 \times 10^{17}$ | $3.6 \times 10^{17} \rightarrow \sim$ |
| CH$^+$ | $5.2 \times 10^{10} \rightarrow 9.3 \times 10^{10}$ | $4.1 \times 10^{11} \rightarrow 1.1 \times 10^{13}$ | $5.7 \times 10^{13} \rightarrow 9.6 \times 10^{13}$ | $5.1 \times 10^{10} \rightarrow 1.9 \times 10^{11}$ |
| CH$_2$ | $1.3 \times 10^{11} \sim$ | $3.3 \times 10^{10} \rightarrow 6.5 \times 10^{11}$ | $4.6 \times 10^{11} \rightarrow 6.6 \times 10^{12}$ | $1.8 \times 10^{13} \rightarrow 3.5 \times 10^{13}$ | $1.3 \times 10^{11} \rightarrow 1.9 \times 10^{11}$ |
| CH$_2$(v = 2) | $2.3 \times 10^{11} \sim$ | $3.8 \times 10^{10} \rightarrow 6.6 \times 10^{11}$ | $1.9 \times 10^{12} \rightarrow 2.1 \times 10^{13}$ | $5.0 \times 10^{13} \rightarrow 2.0 \times 10^{14}$ | $4.7 \times 10^{13} \rightarrow 2.0 \times 10^{11}$ |
| CH | $1.7 \times 10^{13} \sim$ | $2.6 \times 10^{10} \rightarrow 4.4 \times 10^{11}$ | $4.3 \times 10^{11} \rightarrow 8.6 \times 10^{13}$ | $7.7 \times 10^{13} \rightarrow 8.4 \times 10^{13}$ | $3.2 \times 10^{12} \rightarrow 4.8 \times 10^{12}$ |
| OH | $1.1 \times 10^{12} \sim$ | $3.7 \times 10^{10} \rightarrow 3.1 \times 10^{14}$ | $4.6 \times 10^{13} \sim$ | $2.5 \times 10^{15} \rightarrow \sim$ | $1.1 \times 10^{11} \rightarrow 4.4 \times 10^{11}$ |
| H$_2$O | $1.0 \times 10^{11} \sim$ | $2.5 \times 10^{9} \rightarrow 2.3 \times 10^{10}$ | $4.4 \times 10^{10} \sim$ | $1.0 \times 10^{15} \sim$ | $1.1 \times 10^{10} \rightarrow 4.7 \times 10^{10}$ |
| CO | $8.0 \times 10^{12} \sim$ | $8.2 \times 10^{9} \rightarrow 1.6 \times 10^{11}$ | $1.4 \times 10^{13} \sim$ | $2.2 \times 10^{18} \sim$ | $2.0 \times 10^{12} \rightarrow 3.0 \times 10^{12}$ |
| CN | $4.4 \times 10^{11} \sim$ | $1.0 \times 10^{8} \rightarrow 2.4 \times 10^{9}$ | $2.1 \times 10^{11} \rightarrow 2.6 \times 10^{13}$ | $3.2 \times 10^{15} \sim$ | $1.7 \times 10^{10} \rightarrow 4.4 \times 10^{10}$ |
| HCN | $5.4 \times 10^{8} \sim$ | $1.1 \times 10^{8} \rightarrow 2.4 \times 10^{7}$ | $1.5 \times 10^{13} \rightarrow \sim$ | $7.6 \times 10^{15} \rightarrow \sim$ | $9.2 \times 10^{7} \rightarrow 1.7 \times 10^{7}$ |

**Notes.** The adopted elemental abundances for C, N, O, and S are respectively $3.51 \times 10^{-4}$, $7.5 \times 10^{-5}$, $6.23 \times 10^{-4}$, and $9.9 \times 10^{-6}$ in ζ Oph; $1.32 \times 10^{-4}$, $7.5 \times 10^{-5}$, $3.19 \times 10^{-4}$, and $1.85 \times 10^{-5}$ in the “hot PDR” of HD 34078; $1.4 \times 10^{-4}$, $1.0 \times 10^{-4}$, $3.0 \times 10^{-4}$, and $2.8 \times 10^{-5}$ in the Orion Bar; and $1.26 \times 10^{-3}$, $1.91 \times 10^{-4}$, $5.5 \times 10^{-4}$, and $7.94 \times 10^{-5}$ in NGC 7027; and $2.02 \times 10^{-4}$, $5.07 \times 10^{-5}$, $3.67 \times 10^{-4}$, and $9.89 \times 10^{-5}$ in HD 176386.

a The notation $\chi/\chi$ refers to the FUV field $x$ and $y$ at each side of the cloud.

b FUV field at 0.069 pc of a star with $T_s = 198,000$ K and $R_s = 0.075 R_\odot$ radiating as a blackbody.

c FUV field at 0.04 pc of a star with $T_s = 11,300$ K and $R_s = 2.55 R_\odot$ radiating as a blackbody.
limit derived for para H$_2$ by Gerlich 1994) versus the more
conservative value of $4 \times 10^{-16}(T/300)^{-0.2} \text{ cm}^3 \text{ s}^{-1}$ adopted
by us (based on a calculation by Herbst et al. 1985).

We thus find that the reaction of H$_2$ ($v > 0$) and C$^+$ is not able
by itself to explain the large CH$^+$ column densities observed in
diffuse and translucent clouds ($\geq 10^{13} \text{ cm}^{-2}$). Nowadays, the
most popular theories on the CH$^+$ formation in diffuse clouds
invoke the existence of temporary events, such as shocks (Pineau
des Forêts et al. 1986) or turbulence dissipation (Godard et al.
2009), which increase locally the gas kinetic temperature and
allow reaction (1) to proceed. Another possibility is that given
by Federman et al. (1996), who suggest that the ion-neutral
drift produced by Alfvén waves could result in a non-thermal
rate enhancement of ion-neutral reactions, allowing CH$^+$ to be
effectively formed through reaction (1). An enhanced FUV field
has also been proposed as the ultimate cause of CH$^+$ formation
(Snow 1993), a hypothesis that is supported by the fact that in
diffuse clouds the column density of CH$^+$ is well correlated with
rotationally excited H$_2$ ($j \approx 3–5$) (Lambert & Danks 1986),
levels which are to a large extent pumped by FUV fluorescence
in diffuse clouds. An intense FUV field will indeed bring H$_2$
molecules to vibrationally excited states, which in turn will react fast with C$^+$ to form CH$^+$, but when the various magnitudes
are evaluated through a PDR model under a plausible physical
scenario for a diffuse cloud it is found that the abundance of
H$_2$ ($v > 0$) is not high enough to form CH$^+$ with an abundance
close to the typical observed values, as shown in the case of ζ
Oph.

3.2. Dense Interstellar PDRs: Orion Bar

Dense and highly FUV-illuminated clouds are regions where the chemistry of vibrationally excited H$_2$ is expected to play an important role as the fraction of H$_2$ ($v > 0$) is usually large. Here we consider the case of one of the most archetypal dense PDRs which is the Orion Bar, whose parameters (see Table 2) have been taken from van der Wiel et al. (2009). In this case the combination of a high FUV radiation field and a high density ($n_H/\chi \sim 3$) results in a fraction of H$_2$ ($v > 0$) in excess of $10^{-6}$ in the region $A_V = 0.5–1.5$, where hydrogen is still mostly molecular and the gas kinetic temperature is just of a few hundreds of degrees Kelvin (see Figure 5). Thus, the reaction H$_2$ ($v > 0$) + C$^+$ has indeed a great impact on the abundance of CH$^+$ which increases by almost 2 orders of magnitude with respect to that obtained in the standard model.

The existence of an important amount of vibrationally excited H$_2$ in the Orion Bar is supported by astronomical observations (van der Werf et al. 1996). On the other hand, CH$^+$ has not yet been observed but its pure rotational lines lie in the wavelength range of the Herschel Space Observatory. If, as indicated by our model, the formation of CH$^+$ occurs by the reaction of H$_2$ ($v > 0$) and C$^+$, then the spatial distribution of CH$^+$ emission should be well correlated with that of the $v = 1 \rightarrow 0$ S(1) line of H$_2$ observed by van der Werf et al. (1996)

3.3. Planetary Nebulae: NGC 7027

Planetary nebulae are also sources where the chemistry of vibrationally excited H$_2$ can be important since the circumstellar gas is normally exposed to a very high FUV flux which emanates from the hot central white dwarf. A prototype of this kind of object is NGC 7027, which harbors one of the hottest known stars ($T_e \sim 200,000$ K). To model this source we have adopted the physical scenario utilized by Hasegawa et al. (2000) focusing on the dense region (see Table 2). As shown in Figure 6 a large fraction of H$_2$ ($v > 0$) is present in the circumstellar gas of this source ($f^* \sim 10^{-4}–10^{-3}$), and CH$^+$ is readily formed by the reaction of H$_2$ ($v > 0$) and C$^+$ in the regions located close to the star, where C$^+$ reaches its maximum abundance. In these regions the reaction H$_2$ ($v = 0$) + C$^+$ is also an important source of CH$^+$ due to the high temperatures attained.

From the observational point of view the existence of vibrationally excited H$_2$ in NGC 7027 is well established from ISO observations (Bernard Salas et al. 2001), as is the presence of CH$^+$ with a column density of $0.8–2.5 \times 10^{14}$ (Cernicharo et al. 1997), in agreement with the value we get.
Finally, we treat also the case of circumstellar disks surrounding young stars of T Tauri and Herbig Ae/Be type, where the outer disk surface located at just a few AU of the central star is exposed to the strong stellar UV flux. Hot molecular hydrogen both rotationally and vibrationally excited has been observed in various sources of this type (Martín-Zaide et al. 2008). To investigate the importance of the chemistry of vibrationally excited H$_2$ in such environments we take the parameters derived for the warm H$_2$ emitting gas observed by Martin-Zaide et al. (2008) toward the B9 star HD 176836 (see Table 2). As shown in Figure 7 the fraction of vibrationally excited H$_2$ stays around $10^{-7}$–$10^{-6}$ and so the abundance of CH$^+$ is increased by almost one order of magnitude when reactions with excited H$_2$ are included, although in the case of HD 176836 the total column density (see Table 2) remains probably too low to be detected. Some other species experience moderate abundance enhancements as a consequence of the activation of the reaction between H$_2$ ($v > 0$) and C$^+$.  

4. SUMMARY

In this paper, we have investigated the impact of various chemical reactions involving vibrationally excited H$_2$, which have been studied either experimentally or theoretically (concretely those with C$^+$, He$^+$, O, OH, and CN) on the chemical composition of various astronomical regions. Among the reactions considered here that of H$_2$ ($v > 0$) with C$^+$ stands out as the most important one. This reaction becomes the main formation route of the reactive cation CH$^+$ and controls the abundance of some other related species in moderately warm astronomical environments with fractions of vibrationally excited H$_2$ in excess of some $10^{-6}$, conditions which are found to occur in some types of PDR-like regions.

The importance of the chemistry of vibrationally excited H$_2$ has been investigated through PDR models in the diffuse clouds $\xi$ Oph and HD 34078, the Orion Bar, the carbon-rich protoplanetary nebula NGC 7027, and the circumstellar disk HD 176386. The study of $\xi$ Oph indicates that the fraction of H$_2$ ($v > 0$) present ($< 10^{-7}$) is insufficient to form CH$^+$ with the abundance typically observed in diffuse and translucent clouds. On the other hand, in dense and highly FUV illuminated clouds, such as the hot PDR of HD 34078, the Orion Bar and NGC 7027, reactions of vibrationally excited H$_2$ become crucial to determine the global chemical composition. In particular, the reaction H$_2$ ($v > 0$) + C$^+$ becomes the dominant synthetic pathway to CH$^+$ and makes the related species CH$_3^+$ and CH$_3$ reach similar or slightly lower abundances. These two cations however have not yet been observed in any astronomical region—the spectroscopic data of CH$_3^+$ are poorly known (see e.g., Polehampton et al. 2007) while CH$_3$ lacks a permanent dipole moment.  

Other reactions of vibrationally excited H$_2$ not yet studied either experimentally or theoretically, and thus not included here, could become important in regulating the chemical balance of interstellar clouds. For instance, the reactions H$_2$ + C $\rightarrow$ CH + H, H$_2$ + S $\rightarrow$ SH + H, and H$_2$ + S$^+$ $\rightarrow$ SH$^+$ + H are endothermic by 0.99 eV (≈11,500 K), 0.83 eV (≈9600 K), and 0.86 eV (≈9860 K), respectively, and their rate constants have an exponential term of about the value of the endothermicity. This may indicate that, analogously to reaction (1), the internal energy of excited H$_2$ would be effectively used to diminish or overcome the activation barrier so that for H$_2$ ($v > 1$), all these reactions being exothermic, they would proceed at about the collision limit. Experimental or theoretical information on these or other potentially important reactions of vibrationally excited H$_2$ would be of great interest.  

In any case we encourage astrochemists to include the reactions of excited H$_2$ for which kinetic data are available (see Table 1) when modeling the chemistry of regions with an important fraction of vibrationally excited H$_2$. At least the reaction between H$_2$ ($v > 0$) and C$^+$ clearly has an important impact on the global chemical composition of such regions.

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