State-to-state chemistry and rotational excitation of CH$^+$ in photon-dominated regions

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ABSTRACT

We present a detailed theoretical study of the rotational excitation of CH$^+$ due to reactive and nonreactive collisions involving C$^+(2P)$, H$_2$, CH$^+$, H and free electrons. Specifically, the formation of CH$^+$ proceeds through the reaction between C$^+(2P)$ and H$_2$ ($\nu_{H_2}=1,2$), while the collisional (de)excitation and destruction of CH$^+$ is due to collisions with hydrogen atoms and free electrons. State-to-state and initial-state-specific rate coefficients are computed in the kinetic temperature range 10-3000 K for the inelastic, exchange, abstraction and dissociative recombination processes using accurate potential energy surfaces and the best scattering methods. Good agreement, within a factor of 2, is found between the experimental and theoretical thermal rate coefficients, except for the reaction of CH$^+$ with H atoms at kinetic temperatures below 50 K. The full set of collisional and chemical data are then implemented in a radiative transfer model. Our Non-LTE calculations confirm that the formation pumping due to vibrationally excited H$_2$ has a substantial effect on the excitation of CH$^+$ in photon-dominated regions. In addition, we are able to reproduce, within error bars, the far-infrared observations of CH$^+$ toward the Orion Bar and the planetary nebula NGC 7027. Our results further suggest that the population of $\nu_{H_2}=2$ might be significant in the photon-dominated region of NGC 7027.

Key words: ISM: molecules, molecular data, molecular processes, radiative transfer, line: formation

1 INTRODUCTION

The methylidyne ion CH$^+$ was the first molecular ion to be identified from its optical absorption spectra in the diffuse interstellar medium (ISM) [Douglas & Herzberg 1941]. Since then, CH$^+$ absorption has been observed toward many background stars, demonstrating the ubiquity of this simple carbon hydride in the diffuse ISM. The mechanism by which it forms has remained however elusive. Theoretical models have indeed been unable to reproduce the large observed abundance of CH$^+$ in diffuse clouds, [CH$^+$]/[H] $\sim 8 \times 10^{-9}$ (see e.g. [Gedalin & Cernicharo 2013], and references therein). It was for a long time assumed that CH$^+$ is primarily formed by the reaction

$$C^+ + H_2 \rightarrow CH^+ + H.$$ (1)

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This reactions is barrierless but endothermic by 0.398 eV (4620 K) \cite{HierlMorrisViggiano1997}, which is much higher than the kinetic temperatures in ordinary diffuse clouds ($T_K < 100$ K). As a result, non-equilibrium chemistry is necessary to explain the large column densities ($\geq 10^{15}$ cm$^{-2}$) of CH$^+$ observed in the diffuse ISM. The invoked gas heating mechanisms proposed to accelerate reaction (1) include C-type and magnetohydrodynamic shocks, Alfvén waves, turbulent mixing and turbulent dissipation. A recent discussion of these different scenarios in the framework of UV-dominated and turbulence-dominated chemistries can be found in \cite{GodardFalgaronePineauDesForets2014}.

The vast majority of the observed CH$^+$ absorptions arise from the ground rotational level $j = 0$. The first excited level $j = 1$ lies 40.1 K above the ground state and it is not sufficiently populated at the typical density of diffuse clouds where CH$^+$ abounds ($n_H \lesssim 10^3$ cm$^{-3}$). The critical density of the $j = 1 \rightarrow 0$ transition is indeed large, $n_{cr} \sim 4 \times 10^4$ cm$^{-3}$. Rotationally excited levels of CH$^+$ can be significantly populated in the diffuse ISM only in the presence of warm dust emission \cite{oka+13}.

Emission lines from CH$^+$ are less commonly observed but they have been detected in the visible toward the red rectangle (e.g. Bakker et al. 1997) and in the far-infrared toward several sources: the planetary nebula NGC 7027 \cite{cernicharo+97}, the Orion bar \cite{nagy+13,parikka+17}, the Orion BN/KL complex \cite{morris+16}, the massive star-forming region DR21 \cite{falgarone+10}, the infrared galaxy Markarian 231 \cite{van+10} and the disk around the Herbig Be star HD 100546 \cite{thi+11}. The far-infrared lines arise from pure rotational transitions and were detected thanks to the ISO and Herschel space observatories. The largest number of rotational lines were identified in NGC 7027 and in the Orion Bar, which are two prototypical photon-dominated regions (PDRs). In these two sources, the rotational series $j \rightarrow j - 1$ was observed from $j = 1 \rightarrow 0$ at 835.137 GHz up to $j = 6 \rightarrow 5$ at 4976.201 GHz. In such regions the dense gas ($n_H > 10^4$ cm$^{-3}$) is illuminated by a strong far-ultraviolet (FUV) radiation field and a reservoir of H$_2$ re-vibrationally excited by FUV fluorescence can provide an alternative route to overcome the endothermicity of reaction (1) \cite{sternberg+dalgarno93,aguiz+11}. This was evidenced recently in the Orion Bar where a good correlation between CH$^+$ and vibrationally excited H$_2$ was observed by \cite{parikka+17}.

Indeed, it has been shown both experimentally and theoretically that the internal (rotational or vibrational) excitation of H$_2$ can help to reduce or even offset the endothermicity of reaction (1). The rotational and vibrational energies were found to be as effective as the translational energy in promoting the reaction \cite{GerlichDischScherba87,hierl+97,herrea+14}. As a result, the experimental rate coefficient derived by \cite{HierlMorrisViggiano1997} for the reaction of C$^+$ with H$_2$(v$_{H_2}$=1) between 800 and 1300 K is in the range 1-2$\times 10^{-9}$ cm$^3$ s$^{-1}$, in good agreement with the Langevin limit ($1.6 \times 10^{-9}$ cm$^3$ s$^{-1}$). This value represents an enhancement of about 3 orders of magnitude with respect to the rate coefficient of ground-state H$_2$(v$_{H_2}$=0). This finding was confirmed theoretically by two recent independent studies \cite{zanchet+13,herrea+14}. These studies were also able to derive state-to-state rate coefficients and, in particular, \cite{zanchet+13} have provided the first rotationally resolved rate coefficients.

State-resolved rates for the production and loss of CH$^+$ are crucial because the rotational excitation of CH$^+$ is governed by the competition between the radiative processes and the $j$-dependent formation, destruction and collisional excitation processes. Indeed, inelastic collisions with the dominant species, i.e. hydrogen atoms, free electrons and hydrogen molecules, are not faster than the reactive processes. Thus, in contrast to non-reactive molecules such as CO, inelastic collisions can never fully equilibrate the rotational populations of CH$^+$. The CH$^+$ emission spectrum is therefore expected to retain some memory of the $j$-dependent formation process, as discussed in \cite{blach+98}. As a result, when solving the coupled equations of statistical equilibrium and radiative transfer, it is necessary to include state-resolved formation and destruction rates in addition to the usual radiative and inelastic rates. Strong deviations of the level populations from local thermodynamic equilibrium (LTE) are expected in these conditions.

Non-LTE calculations including formation and destruction rates were recently performed to model the CH$^+$ emissions observed toward NGC 7027, the Orion bar and Orion BN/KL \cite{godard+13,parikka+17,zanchet+13,morris+16}. The most complete model is that of \cite{godard+13} which includes the radiative pumping of CH$^+$ vibrational and electronic states by infrared, optical and ultraviolet photons. In all these studies, inelastic data were taken from the state-to-state calculations of Hammani, Owono Owono & Stäuber (2009) and Turpijn, Stecklkin & Voronin (2010) on CH$^+$-He and those of Lim, Rabdán & Tennyson (1999) on CH$^+$-electron, and they were complemented by extrapolations. For the destruction by reactions with H, electrons and H$_2$, generic rates independent of $j$ were assumed, except for CH$^++$H in \cite{godard+13} where the initial-state-specific rate coefficients extracted by \cite{plasil+11} for $j = 0,1,2$ at $T_K \leq 60$ K were used. For the formation by the reaction of C$^+$ with H$_2$, the theoretical data of \cite{zanchet+13} were employed in the most recent studies \cite{zanchet+13,morris+16} while in the previous models of \cite{godard+13} and \cite{nagy+13} the formation rates were expressed as a Boltzmann distribution at an effective formation temperature. The major result of these studies is that in warm and dense PDR conditions, the “formation” or “chemical” pumping via the reaction C$^++$H$_2$(v$_{H_2}$=1) is the dominant source of the rotational excitation of CH$^+$ ($j > 1$). The use of initial-state-specific formation rates (instead of a Boltzmann distribution) was also found to have a substantial impact on the distribution of the highest CH$^+$ levels ($j \geq 4$) \cite{zanchet+13}. Incidentally, the density in the PDR can be one to two orders of magnitude below the values inferred from traditional excitation models \cite{godard+13}. All the models published so far were however hampered by the lack of initial-state-specific rate coefficients for the destruction of CH$^+$ at $T_K > 60$ K. In addition, inelastic data for CH$^+$+H and CH$^+$+H$_2$ were simply scaled from those of CH$^+$+He, which is questionable since collisions with H and H$_2$ are reactive.

Here we provide the first comprehensive set of theo-
retical state-to-state rate coefficients for the inelastic and reactive collisions of CH\(^+\) with hydrogen atoms and free electrons in the temperature range 10-3000 K. This data is computed from state-of-the-art theoretical methods using the most accurate interaction potentials. Theoretical approaches include the time-independent quantum mechanical (TIQM) method, quasi-classical trajectory (QCT) calculations, the R-matrix adiabatic nuclei approach and the multichannel quantum defect theory (MQDT). In addition, new quantum time-dependent (wave-packet) calculations are performed for the formation reaction (1) to extend the data of Zanchet et al. (2013). In the next section, the inelastic and reactive rate coefficients are described with a brief description of the different calculations. In Section 3, these rate coefficients are employed to model the CH\(^+\) emission spectrum for typical PDR physical conditions. Our non-LTE approach includes the time-independent quantum mechanical (TIQM) method, quasi-classical trajectory (QCT) calculations, the R-matrix adiabatic nuclei approach and the multichannel quantum defect theory (MQDT). In addition, new quantum time-dependent (wave-packet) calculations are performed for the formation reaction (1) to extend the data of Zanchet et al. (2013). In those calculations, the cross sections and rate coefficients were determined for the reaction of C\(^+\)(^2P\(^p\)) with H\(_2\) in the ground-state (\(v_{\text{H}_2} = 0, j_{\text{H}_2} = 0\)) and in the first vibrationally excited state (\(v_{\text{H}_2} = 1, j_{\text{H}_2} = 0, 1\)) for temperatures in the range 10-5000 K. In the dynamical calculations, only one adiabatic electronic state was thus considered, neglecting spin-orbit couplings. In order to take them into account, it was assumed that the cross sections for the two C\(^+\)(^2P\(^p\)) states correspond to those calculated in the adiabatic approximation, while the four C\(^+\)(^2P\(^{3/2}\)) states do not contribute to the reaction. The final reaction cross sections was obtained by averaging over all spin-orbit states, considering the proper electronic partition function using the experimental spin-orbit splittings. The reaction cross sections for \(v_{\text{H}_2} = 0\) were found in good agreement with the experimental results of Gerlich, Diisch & Scherbart (1987) while the rate coefficients for \(v_{\text{H}_2} = 1\) were shown to be a factor of \(~3\) smaller than those derived by Hierl, Morris & Viggiano (1997). A very similar result was obtained by Herráez-Aguilar et al. (2014) using a different PES and a different methodology (QCT calculations). Part of the disagreement between theory and experiment was attributed to the contribution of \(v_{\text{H}_2} > 1\) (Zanchet et al. 2013) and to the effect of rotational excitation (Herráez-Aguilar et al. 2014) neglected in the experimental derivation. Full details on the TDWP calculations can be found in Zanchet et al. (2013).

In the present work, the calculations of Zanchet et al. (2013) were extended to the second vibrationally excited state of H\(_2\) (\(v_{\text{H}_2} = 2, j_{\text{H}_2} = 0\)). As we will see below, the population of \(v_{\text{H}_2} = 2\) can be significant in highly FUV illuminated regions. It should be noted that while the rotational excitation of H\(_2\) is crucial in \(v_{\text{H}_2} = 0\) (because reaction (1) is endothermic for \(j_{\text{H}_2} \leq 7\)), it has only a modest impact in vibrationally excited levels \(v_{\text{H}_2} \geq 1\) for which collisions leading to CH\(^+\)(\(v = 0\)) display no threshold. This is illustrated in Fig. 1 below, where we have plotted the rotational distribution of the nascent CH\(^+\)(\(v = 0, j\)) product from the reactions C\(^+\)+-H\(_2\)(\(v_{\text{H}_2} = 1, j_{\text{H}_2} = 0\)), C\(^+\)+-ortho-H\(_2\)(\(v_{\text{H}_2} = 1, j_{\text{H}_2} = 1\)) and C\(^+\)+-para-H\(_2\)(\(v_{\text{H}_2} = 2, j_{\text{H}_2} = 0\)) at a kinetic temperature \(T_k = 500\) K. We can first observe that the rotational state of H\(_2\) \(v_{\text{H}_2} = 1\) (i.e. para or ortho ground-state) has a negligible influence on the CH\(^+\) distribution, as expected. We also observe that the probability distributions for \(v_{\text{H}_2} = 1\) and \(v_{\text{H}_2} = 2\) peak at \(j \sim 6\) and \(j \sim 10\), respectively. These distributions do not follow Maxwell-Boltzmann functions but they have, however, a resemblance to Maxwellian distributions at \(T_f = 1000\) K and \(T_f = 5000\) K, respectively. As the reaction enthalpy is \(~-1500\) K for H\(_2\)(\(v_{\text{H}_2} = 1, j_{\text{H}_2} = 1\)) and \(~-7000\) K for H\(_2\)(\(v_{\text{H}_2} = 2, j_{\text{H}_2} = 0\)), this suggests that about 2/3 of the exothermicity of the reaction is transferred to CH\(^+\) rotation. Thus, although approximate and confusing, the concept of “formation temperature” is not irrelevant. We note also that the effect of kinetic temperature is moderate in the range \(T_k = 10 - 5000\) K: the distribution broadens with increasing temperature but the distribution peak is not shifted.

2 INELASTIC AND REACTIVE RATE COEFFICIENTS

2.1 Formation via C\(^+\) + H\(_2\)

The calculations presented in this section are an extension of the work of Zanchet et al. (2013). In those calculations, the TIQM code ABC (Skouteris, Castillo & Manolopoulos 2001) was combined with a new full-dimensional PES for the ground electronic state of CH\(^+_2\). The ABC code was also checked for the first time against an accurate quan-

![Figure 1. Occupation probability of the nascent CH\(^+\)(\(v = 0, j\)) product from the reaction of C\(^+\) with H\(_2\)(\(v_{\text{H}_2} = 1, j_{\text{H}_2} = 1\)), H\(_2\)(\(v_{\text{H}_2} = 1, j_{\text{H}_2} = 0\)) and H\(_2\)(\(v_{\text{H}_2} = 2, j_{\text{H}_2} = 0\)) at kinetic temperature \(T_k = 500\) K. The Boltzmann distributions at formation temperatures \(T_f = 1000\) and \(5000\) K are plotted as dashed lines.](image-url)
tional threshold of CH are not considered because they lie above the first vibrational temperatures up to $T = 4$. 

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Rate coefficients were determined for CH with a deep potential well. Cross sections and rate coefficients (i.e. averaged over the Boltzmann rotational distributions) were found in good agreement with the experimental data in the range 50-800 K. At lower temperatures, however, the steep fall-off observed experimentally by Plasil et al. (2011) was not reproduced by the calculations of Werfelli et al. (2015), in contrast to other recent theoretical works based on different PESs: Warmbier & Schneider (2011), Grozdanov & McCarroll (2013), Bovino, Grassi & Gianturco (2014), Li, Zhang & Han (2013). However, the analysis by Werfelli et al. (2015) has shown that those PESs have incorrect long-range behaviour and that the seemingly good agreement with the low-temperature data is fortuitous. Full details on the PES and the TIQM calculations can be found in Werfelli et al. (2015).

In the present work, the calculations of Werfelli et al. (2013) were extended to CH$^+$ ($j = 8 - 13$) and kinetic temperatures up to $T_k = 3000$ K. Levels higher than $j = 13$ are not considered because they lie above the first vibrational threshold of CH$^+$ (which opens at $\sim 3700$ K). Since TIQM calculations are computationally highly expensive for CH$^+$ + H, we resorted here to QCT calculations using the same PES as Werfelli et al. (2013). The QCT calculations were performed for 29 values of the collision energy $E_c$ distributed in the range 1-1600 meV, thus allowing us to calculate the rate coefficients in the range 10-3000 K. Batches of 50,000 trajectories were computed for each value of $E_c$ and for each initial rovibrational state ($\nu, j$) of CH$^+$, with $\nu = 0$ and $0 \leq j \leq 13$. For each batch, the maximum impact parameter was adapted to the inelastic collisions. The zero point energy (ZPE) leakage is a well known shortcoming of QCT calculations, and it is even more pronounced as the number of open rovibrational levels decreases. This failure can be corrected with the help of the Gaussian binning (GB) procedure (Bonnet 2013). However, in the case of inelastic processes, the vibrationally adiabatic trajectories give large contributions which overly dominate the GB probabilities (Bonnet 2013). Therefore, we treated the vibrationally adiabatic trajectories with the standard binning procedure, and use the GB procedure for the remaining trajectories. Finally, the QCT rate coefficients were scaled in order to provide an extension up to 3000 K of the quantum rate coefficients previously calculated below 800 K and for $0 \leq j \leq 13$. For $8 \leq j \leq 13$, an average scaling factor was applied.

In Fig. 2 the rate coefficients for the sum of the inelastic (nonreactive) and exchange processes CH$^+$ $(j = 0)$ + H $\rightarrow$ CH$^+$ $(j')$ + H are plotted as functions of the kinetic temperature for $j' = 1 - 8$. We observe a strong increase of the rate coefficients with increasing temperature which mainly reflects the excitation thresholds of the different transitions (e.g. $0 \rightarrow 1$ opens at 40 K). As a result, the transition with $\Delta j = 1$ is largely favoured at low temperature but this propensity holds also at high temperature, indicating that the cross sections follow the energy gap law (at least for $\Delta j \leq 4$).

We have also checked the reliability of the rigid-rotor approximation for the CH$^+$ excitation by H. It was shown recently that this approximation leads to good results in the case of the endothermic OH$^+$ + H reaction on the quartet PES whose minimum is similar to a van der Waals well (Bulut, Lique & Roncero 2015; Stockelkin, Voronin & Ravez 2003) combined with the CH$^+$ PES of Werfelli et al. (2013) where the CH$^+$ bond length was frozen at its equilibrium geometry. As shown in Fig. 3, the rigid-rotor approximation is found to be very inaccurate for CH$^+$ + H. Indeed, although full-dimensional and rigid calculations have similar propensity rules, the cross sections differ by up to one order of magnitude. In the full-dimensional treatment, the largest fraction of the scattering flux is thus directed into the reactive channel, as expected. This illustrates the importance of full-dimensionality for this reactive system. In the right panel, we also compare the present rigid calculations with the rigid-rotor CH$^+$–He data of Turpin, Stockelkin & Voronin (2010). Perhaps surprisingly, the agreement with the full-dimensional CH$^+$+H calculations is much better, in particular above 100 K. This fortuitous agreement is simply due to the much less attractive CH$^+$–He PES.

In Fig. 4 the rate coefficients for the exothermic destruction process CH$^+$ $(j)$+H $\rightarrow$ C$^+$+H$_2$ are plotted as functions of the kinetic temperature and they are compared to the available measurements. As observed by Werfelli et al. (2013), the agreement between the calculated thermal rate coefficient and the experimental data (Federer et al. 1984, 1985; Luca, Borod & Gerlich 2006, Plasil et al. 2011) is good above $T_k = 50$ K. In particular, the decrease of the rate coefficient between 400 and 1200 K is well reproduced by the calculations. At temperatures below 50 K, the experimental results at 12.2, 30 and 40 K were interpreted by Plasil et al. (2011) as a loss of reactivity of the lowest rotational states of CH$^+$. In contrast, we observe here a reactivity increase
with rotational cooling. This was analyzed by Werfelli et al. (2013) as an increase of the probability for a nonreactive or exchange process with increasing rotational excitation. Obviously, further theoretical and experimental efforts are necessary to understand this discrepancy at low temperature, as discussed in Plasil et al. (2011) and Werfelli et al. (2013).

### 2.3 Excitation and destruction by electrons

The rate coefficients for the destruction of CH$^+$ (j → 0) by H as functions of the kinetic temperature. The calculations presented in this section are taken from Hamilton, Faure & Tennyson (2016) for the electron-impact excitation of CH$^+$ and from Epée Epée et al. (in preparation) for the dissociative recombination (DR) of CH$^+$ with electrons. In the calculations of Hamilton et al. (2016), the molecular R-matrix theory was combined with the adiabatic nuclei rotation (ANR) approximation. Inelastic cross sections and rate coefficients were determined for CH$^+$ (j = 0 – 11) and kinetic temperatures in the range 1-3000 K. No experimental inelastic data is available for this system but we note that the same methodology was applied with success to HD$^+$ for which theoretical rate coefficients were found comparable to within 30% with those resulting from a fit of experimental cooling curves (Shafir et al. 2009). Very good agreement with the MQDT calculations of Motapon et al. (2014) for HD$^+$ and those of Epée Epée et al. (2016) for H$_2^+$ was also observed. In the calculations of Epée Epée et al. (in preparation), the MQDT formalism was employed: based on the diabatic potential energy curves and the interaction between the ionization and the dissociation continua within the $^2\Pi$ symmetry used by Carata et al. (2000), we have computed the interaction, reaction and scattering matrices, and produced the DR cross sections for the 11 lowest rotational levels of CH$^+$ in its ground electronic and vibrational state. Rate coefficients were determined for the DR of CH$^+$ (j = 0 – 10) at kinetic temperatures between 10 and 3000 K. The CH$^+$ thermal DR cross section (after convolution with the experimental resolution) was found in satisfactory agreement with the measurements of Amitay et al. (1996) below 100 meV, and especially below 50 meV. Full details will be published elsewhere (Epée Epée et al., in preparation).

The rate coefficients for the inelastic process CH$^+$ (j = 0) + e$^-\rightarrow$ CH$^+$ (j') + e$^-$ are discussed in Hamilton et al. (2016) where full details can be found. In their Fig. 3, the temperature dependences of the rate coefficients are found to be similar to those observed here for CH$^+$ + H (Fig. 2) due to the threshold effects. Dipolar transitions $\Delta j = 1$ were found to be preferred, as expected for a strongly polar target. We note that this is in contrast with the previous R-matrix results of Lim et al. (1999) who found the cross sections for the $\Delta j = 2$ transitions to be greater than $\Delta j = 1$ transitions. This difference was attributed by Hamilton et al. (2016) to the improved treatment of polarization in the new calculations.

In Fig. 5, the initial-state-specific DR rate coefficients are plotted as functions of the kinetic temperature. These rate coefficients were obtained by averaging the cross sections over isotropic Maxwell-Boltzmann velocity distributions. The thermal average at a rotational temperature of 300 K is also shown and it is compared to two sets of experimental rate coefficients. The first was obtained from a thermal average of the DR cross sections measured by Amitay et al. (1996), where the ions were assumed to be thermalized at the ambient temperature of the storage ring (300 K). The second is the experimental recommendation of Mitchell (1990). This later is based on the merged-beam data of Mitchell & McGowan (1978) (divided by 2 to correct for a calibration error). The recommendation of Mitchell (1990) is found to exceed the results of Amitay et al. (1996) by about...
Figure 5. Rate coefficients for the destruction of CH$^+(j)$ by electrons as functions of the kinetic temperature. The initial-state-specific and 300 K thermal rate coefficients from the present work are compared to the experimental results of Amitay et al. (1996) and Mitchell (1990).

3 RADIATIVE TRANSFER MODEL

In order to illustrate the impact of the newly computed rate coefficients for the CH$^+$ formation, excitation and destruction, we now implement these data in a non-LTE radiative transfer model of CH$^+$ excitation in PDR conditions. PDRs are predominantly neutral regions of the interstellar medium where the gas is exposed to FUV radiation fields ($\sim 6-13.6$ eV). PDRs typically occur at the boundaries of planetary nebulae, on the edges of molecular clouds and in the nuclei of starburst and active galaxies (Sternberg & Dalgarno 1993). A PDR thus starts at the fully ionized “HII” region where only far-ultraviolet radiation penetrates the neutral gas, i.e. stellar photons that cannot ionize hydrogen atoms but do ionize elements with low ionization potential (< 13.6 eV) such as carbon. The C$^+$ column density thus increases with the intensity of FUV radiation and it decreases with gas density. Inside the PDR, the FUV photon flux is indeed limited by H$^2$ and dust absorption. Beyond the edge of the C$^+$ zone, carbon is rapidly incorporated into CO. PDR models indicate that the CH$^+$ abundance peaks at visual extinctions $A_V \sim 0.1-1$ where the carbon is fully ionized and where the amount of vibrationally excited H$_2$ is high ($f^* = n(\nu_H > 0)/n(\nu_H = 0) > 10^{-6}$) (Agúndez et al. 2014; Godard & Cornichard 2013; Nagy et al. 2013). In this zone, hydrogen is predominantly in atomic form, most of the electrons are provided by the ionization of carbon atom, the kinetic temperature $T_k$ is a few hundreds of Kelvin and the thermal pressure ($P/k_B = n_kT_k$) is about $10^8$ K cm$^{-3}$. Obviously, the physical conditions in PDRs encompass a range of temperatures and densities with a rather complex morphology, as revealed recently with ALMA (Geicoerebea et al. 2016). In the following, however, we will assume that CH$^+$ probes a region with homogeneous density and temperature, corresponding to the “hot gas at average density” described by Nagy et al. (2017) for the Orion Bar.

As explained in the Introduction, since CH$^+$ is destroyed by hydrogen atoms and electrons on a similar time scale as it is rotationally equilibrated (by the same colliders), the chemical formation and destruction rates need to be included when computing the statistical equilibrium equation (e.g. van der Tak et al. 2000):

$$\frac{dn_i}{dt} = \sum_{ij} n_i P_{ij} - \sum_{ij} n_j P_{ij} + F_i - n_i D_i = 0. \quad (2)$$

In this equation, $N$ is the number of levels considered, $n_i$ is the level population of level $i$, $P_{ij}$, and $P_{ij}$ are the populating and depopulating rates:

$$P_{ij} = \begin{cases} A_{ij} + B_{ij}J_0 + C_{ij} & (i > j) \\ B_{ij}J_0 + C_{ij} & (i < j), \end{cases} \quad (3)$$

and $F_i$ and $D_i$ are the state-resolved formation and destruction rates, respectively, of level $n_i$. In Eq. [3], $J_0$ denotes the specific intensity integrated over line profile and solid angle and averaged over all directions. The proportionality rates $A_{ij}$ and $B_{ij}$ are the Einstein coefficients for spontaneous and stimulated emission, respectively, and the $C_{ij}$ are the collisional rates, i.e. the product of the collisional rate coefficients (in cm$^3$s$^{-1}$) and the collider density (in cm$^{-3}$), summed over all possible collision partners (here $H$ and $e^-$). Note that in Eq. [3] the notation $i > j$ means all states below an energy higher than the energy of level $j$.

The main difficulty in solving the radiative transfer problem is the interdependence between the level populations and the local radiation field. Among approximate methods, the escape probability technique (e.g. Castor 1970) is widely employed. It is not adapted to model inhomogeneous sources, for which more sophisticated treatments are available (see e.g. Lambert et al. 2013 and references therein), but it is very useful in describing global average properties. In the present work, we have employed the public version of the RADEX code\footnote{http://home.strw.leidenuniv.nl/~moldata/radex.html} which uses the escape probability formulation assuming an isothermal and homogeneous medium. In its public version, the formation and destruction rates are assumed to be zero. We have therefore implemented in RADEX the inclusion of the source ($F_i$ in cm$^3$s$^{-1}$) and sink ($D_i$ in s$^{-1}$) terms, which requires only minor modifications. It should be noted that only the relative values of $F_i$ matter since the CH$^+$ column density is fixed within RADEX. As a result, the column density of C$^+$ and H$_2(\nu_H > 2)$ are implicit...
parameters in our calculations. The adopted formation rates correspond to $H_2$ in the initial state ($\nu_{H_2} = 1, j_{H_2} = 1$) or, alternatively, ($\nu_{H_2} = 2, j_{H_2} = 0$) (see below).

3.1 Prototypical PDR

The input parameters to RADEX are the kinetic temperature, $T_k$, the column density of $\text{CH}^+$, $N(\text{CH}^+)$, the line width, $\Delta v$, and the density of the colliding partners, $n_H$ and $n(e^-)$. For a prototypical PDR, the thermal pressure is of the order of $10^6$ K cm$^{-3}$ (see above). Here the density was set at $n_H = 2 \times 10^5$ cm$^{-3}$ and the kinetic temperature at $T_k = 500$ K. We adopted a typical electron fraction of $x_e = n(e^-)/n_H = 10^{-4}$, as expected if carbon is fully ionized (for a standard ISM carbon elemental abundance).

The line width was fixed at 5 kms$^{-1}$ as observed in the Orion Bar (Nagy et al. 2013) and the $\text{CH}^+$ column density was set at $10^{14}$ cm$^{-2}$, corresponding to an average $\text{CH}^+$ abundance of $\sim 10^{-8}$. Finally, we assumed the cosmic microwave background (CMB) as the only background radiation field with a temperature of 2.73 K. It was indeed shown by Godard & Cernicharo (2013) that radiative pumping has only a minor influence on the $\text{CH}^+$ rotational distribution.

In Fig. 6, the line fluxes of the rotational series $j \to j - 1$ from $j = 1 \to 0$ to $j = 9 \to 8$ are plotted as functions of the upper level energies for three different calculations: in the first, the public version of RADEX was employed, which entirely neglects the formation and destruction rates of $\text{CH}^+$. The rotational distribution of $\text{CH}^+$ is therefore established only through inelastic collisions with hydrogen atoms and free electrons. In the second calculation, the full model, which considers the formation of $\text{CH}^+$ via $\text{C}^++\text{H}_2(\nu_{H_2} = 1, j_{H_2} = 1)$ and its destruction via reactive collisions with hydrogen atoms and electrons, is employed. In the third calculation, the formation rates are those corresponding to $\text{H}_2(\nu_{H_2} = 2, j_{H_2} = 0)$. The relative populations of the vibrationally excited states of $\text{H}_2$ are not known with precision but the state $\nu_{H_2} = 2$ can reach a population of $\sim 0.3 - 0.5$ with respect to the $\nu_{H_2} = 1$ state, e.g. in the Orion bar (van der Werf et al. 1996, Walmsley et al. 2000).

The $\nu_{H_2} = 2$ state can therefore play an important role in the chemical pumping of $\text{CH}^+$. We can first observe in Fig. 6 that the inclusion of formation and destruction rates (“full model”) increases the fluxes of the lines by at least a factor of 2 and up to two orders of magnitude. This clearly illustrates the importance of chemical pumping, even for the lowest $j = 1 \to 0$ transition. The impact of the $\nu_{H_2} = 2$ state is to further increase the line fluxes, especially for transitions above $j = 4$. This is easily explained by looking at the rotational distributions of the nascent $\text{CH}^+(\nu = 0, j)$ in Fig. 7 the probability for $\nu_{H_2} = 2$ peaks at higher $j$ than $\nu_{H_2} = 1$ and this initial hotter distribution translates into a larger final excitation. This demonstrates that the memory of the $\text{CH}^+$ formation process is transferred to, and preserved in the rotational distribution. In other words, the radiative cascade subsequent to the initial formation of $\text{CH}^+$ is dominant over the pure inelastic (excitation and de-excitation) processes.

3.2 The Orion Bar

The Orion Bar PDR is the archetypal edge-on molecular cloud surface illuminated by FUV radiation from nearby massive stars. The presence of vibrationally excited $\text{H}_2$ in this source is supported by infrared observations of the $\nu_{H_2} = 1 \to 0$ and $\nu_{H_2} = 2 \to 1$ transitions (van der Werf et al. 1996). $\text{CH}^+$ was first detected in the Orion Bar by Naylor et al. (2010) and Habart et al. (2010), based on Herschel-SPICE maps of the $j = 1 \to 0$ transition. These studies were then extended thanks to Herschel-HIFI and Herschel-PACS data with the detection of the full rotational series up to $j = 6 \to 5$ by Nagy et al. (2013). Recently, the spatial distribution of $\text{CH}^+$ was found to be well correlated with that of the $\nu_{H_2} = 1 \to 0$ line of $\text{H}_2$ in this source (Parikka et al. 2017), as predicted by Agúndez et al. (2010). Previous non-LTE models including chemical pumping for the Orion Bar can be found in Godard & Cernicharo (2013), Zanich et al. (2013) and Nagy et al. (2013).

In our non-LTE calculations, we adopted the same physical conditions as for the above prototypical PDR, except that the $\text{CH}^+$ column density is a free parameter adjusted to best reproduce the observations of Nagy et al. (2013), assuming a unit filling factor. Very good agreement is observed in Fig. 8 between the model ($\nu_{H_2} = 1$) and the observations for a $\text{CH}^+$ column density of $9 \times 10^{13}$ cm$^{-2}$, corresponding to a column density per unit line width of $1.8 \times 10^{13}$ cm$^{-2}$ (km s$^{-1}$)$^{-1}$. Indeed, the calculations agree within error bars with Herschel data, except for the highest transition. This column density is in excellent agreement with that derived by Morris et al. (2010) for the Herschel-HIFI lines reported in Table 2 of Nagy et al. (2013) were corrected for main beam efficiencies (Nagy, Z. private communication).

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Orion BN/KL average. It is however a factor of 10 lower than the value of Nagy et al. (2013) for the Orion Bar. These authors have employed similar physical conditions but lower densities and different collisional and chemical rates, which likely explains the differences and illustrates the importance of accurate microphysics data. In Fig. 7, we have also reported our results when the formation rates are those for $H_2(νH_2 = 2, JH_2 = 0)$. As expected, these rates produce a hotter rotational distribution (see also Fig. 8) and the flux of the lines $j = 5 → 4$ and $j = 6 → 5$ is higher than that observed, suggesting that the relative population of $νH_2 = 2$ is not large in the Orion Bar. We note, finally, that the contribution of electron collisions is small at an electron fraction $x_e = 10^{-4}$; the largest effect is a 11% increase in the intensity of the ground-state $j = 1 → 0$ transition, as observed by Nagy et al. (2013). The excitation and destruction of $CH^+$ in this source is therefore dominated by hydrogen collisions.

3.3 NGC 7027

NGC 7027 is a prototypical young planetary nebula in which the circumstellar gas is exposed to a high FUV flux emanating from the hot central white dwarf. A large fraction of vibrationally excited $H_2$ ($f_v^+ ∼ 10^{-3}$) is predicted for this source (Agúndez et al. 2010). The presence of excited $H_2$ was established by ISO observations of several $νH_2 = 1 → 0$ transitions (Bernard-Salas et al. 2001). $CH^+$ was discovered in this source by Cernicharo et al. (1997) with the ISO detection of five rotational lines from $j = 2 → 1$ to $j = 6 → 5$. The ground-state line $j = 1 → 0$ was detected more recently with Herschel-SPIRE by Wesson et al. (2010). These authors have shown that the six rotational lines cannot be fitted by a single excitation temperature. The first non-LTE model including chemical pumping for NGC 7027 was presented by Godard & Cernicharo (2013).

In our non-LTE calculations, we adopted the same hydrogen density and kinetic temperature as for the above prototypical PDR but the other parameters were modified as follows: the electron fraction was increased to $x_e = 10^{-3}$ to account for the higher elemental carbon abundance in this carbon rich circumstellar envelope (Godard & Cernicharo 2013), and the line width was set at 30 km s$^{-1}$, as in Cernicharo et al. (1997). We also assumed that the size of the CH$^+$ emission in the PDR is 10'' (Cox et al. 2002). Finally, the CH$^+$ column density is again the free parameter adjusted to best reproduce the ISO and Herschel observations. Note that the flux toward NGC 7027 was measured in W cm$^{-2}$ (not in K km s$^{-1}$) so that it does not decline monotonically with increasing upper level energy. Good agreement is observed in Fig. 8 between the model and the observations, although the fluxes of the highest transitions $j = 5 → 4$ and $j = 6 → 5$ are underproduced when $H_2$ is initially in $ν_2 = 1$. The best model is obtained for a large CH$^+$ column density of $2 \times 10^{15}$ cm$^{-2}$, corresponding to a column density per unit line width of $6.7 \times 10^{13}$ cm$^{-2}$ (km s$^{-1}$)$^{-1}$, in good agreement with Godard & Cernicharo (2013). Fig. 8 also reports our results when the formation rates are those for $H_2(νH_2 = 2, JH_2 = 0)$. The agreement with ISO observations is now within error bars. This suggests that the relative population of the state $νH_2 = 2$ could be large in the PDR of NGC 7027. The observations of higher frequency transitions of CH$^+$ ($j = 7 → 6$, etc.) might help to confirm this result. Finally, we note that the contribution of electron collisions is substantial here at an electron fraction $x_e = 10^{-3}$ cm$^{-3}$: a 75% increase in the intensity of the ground-state $j = 1 → 0$ transition was observed. This effect decreases for higher transitions but electrons still contribute above 10% for the $j = 4 → 3$ transition. As a result, electrons compete with hydrogen atoms for the excitation and destruction of CH$^+$ in this carbon-rich circumstellar envelope.
4 CONCLUSION

We have presented a detailed theoretical study of the rotational excitation of CH$^+$ due to chemical pumping, excitation and destruction. The investigated colliders were hydrogen atoms and free electrons. State-to-state and initial-state-specific rate coefficients were computed for the inelastic, exchange, abstraction and dissociative recombination processes using the best available potential energy surfaces and scattering methods. State-to-state rate coefficients were also computed for the formation reaction, $C^+ (^2P) + H_2 (v_{\text{rot}}, j_{\text{rot}}) \rightarrow CH^+ + H$ by extending the calculations of Zanchet et al. (2013) to the vibrationally excited state ($v_{\text{rot}} = 2, j_{\text{rot}} = 0$). Good agreement with available experimental thermal rate coefficients was observed, except for the reaction abstraction $CH^+ + H$ at low temperature ($< 50$ K). The full set of collisional and chemical data were then implemented in a radiative transfer model based on the escape probability formalism. These non-LTE calculations have confirmed previous studies that suggested that chemical pumping has a substantial effect on the excitation of CH$^+$ in PDRs (Godard & Cernicharo 2013; Nagy et al. 2012; Zanchet et al. 2013). However, in contrast to these previous works, we have employed for the first time a comprehensive theoretical set of fully state-to-state data. Our non-LTE model was applied to typical PDR conditions and, in particular, to two prototypical sources: the Orion Bar and the planetary nebula NGC 7027. We were able to reproduce, within error bars, the ISO and Herschel measurements by adjusting the CH$^+$ column density as a single free parameter.

Obviously, there is no unique solution and this work can be further improved e.g. by computing self-consistently the CH$^+$ abundance, instead of fixing its column density. The impact of the H$_2$ rotational distribution within the different vibrational manifolds should be also investigated. This will require to extend the calculations on $C^+ (^2P) + H_2 (v_{\text{rot}}, j_{\text{rot}})$ to higher rotational levels $j_{\text{rot}} > 1$, of particular importance in the ground vibrational state $v_{\text{rot}} = 0$. Collisions between CH$^+$ and H$_2$ should be also considered. We have assumed in the present work that hydrogen is in atomic form in the region of maximum CH$^+$ abundance. However, a non-negligible molecular hydrogen fraction is necessary to form CH$^+$ from C$^+$ + H$_2$. The knowledge of state-to-state rate coefficients for the CH$^+$ + H$_2$ collisions might even provide constraints to the H$_2$ fraction. Calculations of the PES for the electronic ground state of CH$^+$ are in progress in Bordeaux (Halvick and co-workers). Finally, the generalization of this work to the excitation of other reactive species such as OH$^+$ and SH$^+$, for which state-resolved formation rates are becoming available (Gómez-Carrasco et al. 2013; Zanchet, Roncerò & Bulut 2014), will be presented in future works.

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