FORMATION PUMPING OF MOLECULAR HYDROGEN IN DARK CLOUDS

Farahjabeen Islam 1, Cesare Cecchi-Pestellini 2, Serena Viti 1, and Silvia Casu 2

1 University College London, Department of Physics and Astronomy, Gower Street, London WC1E 6BT, UK; fislam@star.ucl.ac.uk, sv@star.ucl.ac.uk
2 INAF-Osservatorio Astronomico di Cagliari, Strada n.54, Loc. Poggio dei Pini, 09012 Capoterra (CA), Italy; ccp@caastro.it, scasu@caastro.it

ABSTRACT

Many theoretical and laboratory studies predict H 2 to be formed in highly excited rovibrational states. The consequent relaxation of excited levels via a cascade of infrared transitions might be observable in emission from suitable interstellar regions. In this work, we model H 2 formation pumping in standard dense clouds, taking into account the H/H 2 transition zone, through an accurate description of chemistry and radiative transfer. The model includes recent laboratory data on H 2 formation, as well as the effects of the interstellar UV field, predicting the populations of gas-phase H 2 molecules and their IR emission spectra. Calculations suggest that some vibrationally excited states of H 2 might be detectable toward lines of sight where significant destruction of H 2 occurs, such as X-ray sources, and provides a possible explanation as to why observational attempts resulted in no detections reported to date.

Key words: infrared: ISM – ISM: lines and bands – ISM: molecules – molecular processes

Online-only material: color figure

1. INTRODUCTION

By far the most abundant element in the universe is hydrogen. Consequently, H 2 is the most abundant molecule and is the dominant collision partner in dark interstellar clouds. Dust grain surfaces act as heterogeneous catalysts in the formation of H 2 molecules from atomic hydrogen (Gould & Salpeter 1963; Hollenbach & Salpeter 1979). Beyond this general consensus, the actual formation mechanism remains elusive and the internal energy distribution of the nascent hydrogen molecule is unknown. During formation, the H 2 binding energy ΔE b = 4.476 eV must be partitioned between the rovibrational excitation and translational energy of the nascent molecule and heating of the dust grain (Duley & Williams 1993). By studying the formation pumping of molecular hydrogen, namely the rovibrational distribution of nascent H 2 molecules, we can constrain interstellar chemistry both in the gas phase and on grain surfaces.

If the internal and translational energies of nascent molecules are relatively small, then significant grain heating must take place, which may lead to the desorption of volatile molecules from the dust grain surface (Duley & Williams 1993; Roberts et al. 2007). The H 2 internal energy distribution could have a significant impact on the chemistry occurring in the interstellar medium (ISM) because vibrationally excited H 2 will increase the overall energy budget of gas-phase processes. There have been many theoretical and laboratory studies that predict H 2 to be formed in highly excited rovibrational states (e.g., Sizun et al. 2010; Martinazzo & Tantardini 2006 and references therein). It is possible that this formation pumping may be observable in the infrared (IR) spectra of H 2 molecules.

The effects induced in the IR spectrum of H 2 by rovibrational excitation of nascent molecules were first considered by Black & Dalgarno (1976), who employed a formation pumping model in which equipartition of the H–H binding energy released was arbitrarily assumed. In this model, the binding energy is split equally between the internal energy of the molecule, its translational energy on desorption from the grain surface, and the heat imparted to the grain lattice. The molecule is formed at an effective temperature T f ∼ 9000 K. The internal energy is spread with a Boltzmann distribution throughout the rovibrational levels, with the ortho-to-para ratio (OPR) being approximately 3. Subsequently, several classical molecular dynamics and quantum mechanical calculations have been carried out for H 2 formation on surfaces whose chemical compositions are analogous to interstellar dust grains, but the results have shown a wide dispersion in predicted vibrational distributions.

Draine & Bertoldi (1996) proposed a rovibrational distribution function that boosts the populations of vibrational states relative to the population of rotational states. The formation temperature is T f = 5 × 10 4 K, the OPR is ∼ 2.8, and the mean vibrational and rotational levels are 5.3 and 8.7, respectively. Duley & Williams (1986) suggested a mechanism which differs from previous proposals in the method of stabilization of the reacting complex. The stabilization energy (∼0.4 eV) is transferred to a surface band, whose energy is that of the OH stretching vibration. The Duley & Williams (1986) model predicts that the H 2 molecule on formation is ejected into the gas vibrationally excited (ν ~ 6, 7) but rotationally cool (J = 0, 1). The Duley & Williams (1986) and Black & Dalgarno (1976) models were employed by Le Bourlot et al. (1995) to generate H 2 IR spectra. Le Bourlot et al. (1995) presented results for another formation pumping scheme, which postulates that no energy is transferred to translation or to dust lattice modes. Thus, H 2 is formed in its highest vibrational level, ν = 14, close to the dissociation threshold, with J = 2 and 3 weighted by the nuclear spin statistics. H 2 spectra were also presented by Tine et al. (2003) based on ER quantum calculations by Farebrother et al. (2000) and Meijer et al. (2001). Finally, Takahashi & Uehara (2001) constructed formation pumping models for hydrogen molecules newly formed on icy mantles, carbonaceous and silicate dust, based on classical and quantum theoretical studies of molecular dynamics (Parneix & Brechignac 1998; Takahashi et al. 1999; Meijer et al. 2001). All these models provide characteristic spectral patterns, which may be used to discriminate between the H 2 formation pumping mechanisms via astronomical observations.

Duley & Williams (1993) suggested that the most favorable location to detect formation pumping would be from dense,
dark, quiescent, starless cores, where ultraviolet (UV) pumping is minimized. This suggestion is supported by Takahashi & Uehara (2001) and Tiné et al. (2003), who state that the relative emissivities of lines due to formation pumping in dense clouds can be a factor of 500 greater than in diffuse clouds. However, dark cloud observations have as yet failed to detect any spectral lines due to formation pumping (e.g., Tiné et al. 2003 and Congiu et al. 2009). In a laboratory study, Congiu et al. (2009) consider the thermalization of nascent H2 molecules on the surface of dust grains, either within the porous structure of the grain or via collisions with other adsorbates in the thick icy mantle surrounding dust grains in dark clouds. Furthermore, spectra may not be observable due to the lack of an efficient mechanism to supply H atoms, such as a very high cosmic-ray ionization rate $\zeta \sim 10^{-14} \text{s}^{-1}$ to dissociate H2 molecules, as found by Le Bourlot et al. (1995).

In this paper, we present a new experimentally derived formation pumping model constructed from the results of the UCL Cosmic Dust Experiment (Perry & Price 2003; Creighan et al. 2006), and we compute IR emission spectra of H2 expected in interstellar clouds. The H2 formation pumping model is coupled with an accurate description of both radiative transfer and chemistry in stratified dark clouds. Section 2 contains a description of the formation pumping excitation model employed in the calculations. In Section 3, we summarize the method and the procedures followed using different formation pumping models to calculate the complete rovibrational distribution of H2 formed on dust grains. H2 emission spectra are presented in Section 4. We discuss observational implications and present our conclusions in Section 5.

2. H2 FORMATION PUMPING

2.1. The Experiment

The rovibrational excitation of molecular hydrogen desorbed from surfaces can be measured experimentally. A quantitative partitioning of the excitation between vibrational states has been investigated by the UCL Cosmic Dust Experiment, which probes the distribution of the rotational states within each vibrational manifold (Perry & Price 2003; Creighan et al. 2006). The experiment studies the formation of molecular hydrogen, primarily HD, on a highly oriented pyrolitic graphite (HOPG) surface under ultrahigh vacuum, following continuous irradiation of the surface by H and D atoms. The nascent HD (or H2J) molecule will desorb in rovibrational states $(v, J)$ of the ground electronic state. Hydrogen molecules are state selectively ionized using laser-induced resonance enhanced multi-photon ionization spectroscopy. The relative populations of the rovibrational states are then derived from ion yields.

The experiment probes HD preferentially to H2 (or D2) because there is a significant amount of undissociated H2 originating from the H atom source. As studies of $v = 1$ and 2 for the isotopic species revealed very similar flux densities and rotational distributions for both HD and H2 molecules (Creighan et al. 2006), we extrapolate the HD $v = 3–7$ data to obtain the rovibrational distribution of nascent H2. However, nascent HD in the $v = 0$ state could not be detected above the signal from background gas in the vacuum chamber (see Creighan et al. 2006). As a modest estimate of the internal excitation of H2, we set the $v = 0$ populations to be equal to the populations of the $v = 1$ states. Since this is an arbitrary choice, H2 emission spectra have been generated with the $v = 0$ states both significantly more and less populated than expected. The sensitivity of the H2 spectra to the error in the population of the $v = 0$ states is discussed further in Section 4.

HD formed on HOPG held at 15 K has been found in rovibrational states $(v, J) = (1–2, 0–4), (3–5, 0–6), (6, 0–4)$, and $(7, 0–3)$ (Creighan et al. 2006; Islam et al. 2007; Latimer et al. 2008). The rovibrational distribution of HD peaks at $v = 4, J = 1$. The total vibrational population, found by summing the relative rotational populations, approximately doubles with subsequent $v$ state up to $v = 4$, then falling sharply at $v = 5$. This indicates that the vibrational distribution differs dramatically from a Boltzmann distribution. Examination of Boltzmann plots reveals that the rotational distributions within each $v$ state also slightly deviate from a Boltzmann distribution.

Translational energy of the molecule is known to have an upper limit of 0.9 eV (Creighan et al. 2006). Such a low translational energy of nascent hydrogen molecules has been observed by other experimental studies (Vidal et al. 2004). From assuming that the $v = 0$ populations are roughly equal to the $v = 1$ populations, the rovibrational distribution corresponds to an internal excitation of 1.74 eV, with at least 41% of the HD binding energy flowing into the surface.

In order to retain any deviation from the Boltzmann distribution, we scale the HD rotational populations by the appropriate nuclear spin statistical weight $g_N$ to obtain the rotational populations of H2. Assuming the OPR of H2 formation in space to be approximately 3 (e.g., Draine & Bertoldi 1996 and Takahashi 2001), we set $g_N = 1$ and 3 for even $J$ and odd $J$, respectively. By scaling the rovibrational populations from HD to H2, we note that although the rovibrational distribution is preserved, the average energy of the molecule has marginally increased. This change in internal energy is due to the energy levels of H2 being more spaced out within the potential well, as H2 is lighter than HD. Thus, the resulting average energy of H2 is 1.95 eV. Three-body coupling between the two H atoms and a quantum defect within the substrate may be strong enough to randomize the spin orientation of the newly formed molecule. However, we do not expect there to be as many defects on our HOPG surface as on a real interstellar dust grain (see Section 2.2). Experiments conducted probing the rovibrational distribution of H2 as well as HD (Creighan et al. 2006) show that there is no significant difference in vibrational level populations for H2 and HD formed in $v = 1$ and 2. Also, rotational temperatures of H2 and HD within each vibrational state were found to be similar ($\sim 300$ K), taking an OPR equal to 3, for H2. Furthermore, Takahashi & Uehara (2001) calculate that the OPR of newly formed H2 is nearly 3 on silicate, carbonaceous, and icy surfaces. Thus, we feel that statistical weighting is a good approximation.

The relative populations of all the states are then normalized to obtain $\delta_{v, J}$, the fraction of H2 formed on grain surfaces that leaves the grain in level $(v, J)$, such that $\sum_{v, J} \delta_{v, J} = 1$. The formation pumping population distribution of H2 used throughout this paper is shown in Figure 1 and reported in Table 1.

2.2. Astrophysical Surfaces

Astrophysical surfaces are of course likely to be very different from the HOPG surface used in the UCL Cosmic Dust Experiment. Important characteristics of an interstellar dust grain are chemical composition, fraction of crystallization, roughness, state of charge, and temperature. Therefore, it is important to discuss how the adopted representation of the H2 formation pumping population distribution may be related to the properties of interstellar grain surfaces.
shown that H\textsubscript{2} forms rovibrationally excited on carbon surfaces, other than which quantifies the rovibrational distribution of nascent molecules on a non-porous surface. Unfortunately, there is no work to date which gives the molecular composition or degree of order of the surface, given a temperature-programmed desorption (TPD) experiment and Amiaud et al. (2007) have detected nascent molecules in vibrational states \(v = 1\)–7. The detection of vibrationally excited molecules in the two experiments implies that the formation process on HOPG and NP ASW may be similar. Consequently, internal excitation of nascent hydrogen molecules may not significantly depend on the chemical composition or degree of order of the surface, given a non-porous surface. Unfortunately, there is no work to date which quantifies the rovibrational distribution of nascent molecular hydrogen on astrophysically relevant surfaces, other than the UCL Cosmic Dust Experiment and Amiaud et al. (2007) have shown that H\textsubscript{2} forms vibrationally excited \((v \geq 2)\) on non-porous amorphous ice (NP ASW) held at 8–30 K. Therefore, vibrational excitation of nascent molecules seems to occur regardless of crystallization fraction. Both the UCL Cosmic Dust Experiment and Amiaud et al. (2007) (see the text).

The experimental results utilized in this work (Creighan et al. 2006; Islam et al. 2007; Latimer et al. 2008) show that HD forms vibrationally excited on HOPG, which is a non-porous, well-ordered crystalline structure. Amiaud et al. (2007) have shown that D\textsubscript{2} forms vibrationally excited \((v \geq 2)\) on non-porous amorphous ice (NP ASW) held at 8–30 K. Therefore, vibrational excitation of nascent molecules seems to occur regardless of crystallization fraction. Both the UCL Cosmic Dust Experiment and Amiaud et al. (2007) have shown that HD forms vibrationally excited on carbon surfaces at temperatures of 90–300 K, but these temperatures are too high to simulate the majority of interstellar conditions. Vidalí et al. (2006) have found that the recombination of hydrogen is efficient on carbon surfaces at temperatures of 11–18 K, on olivine surfaces at temperatures of 6–9 K, on low-density amorphous ice surfaces at temperatures of 11–15 K, and on high-density amorphous ice surfaces at temperatures of 14–18 K. However, the temperature-programmed desorption (TPD) experiments of Vidalí et al. (2006) do not probe the rovibrational distribution of nascent molecules.

The roughness of a dust grain may also affect the rovibrational distribution of nascent molecules, as defects in the crystalline structure may allow atoms to chemisorb, hence bond more strongly with the graphite surface. There is a 0.2 eV barrier to chemisorption on graphite surfaces (Zecho et al. 2002), which arises from carbon atoms having to pucker out of the graphite sheet to bond with incident hydrogen atoms. Hence, for the UCL Cosmic Dust Experiment, where the incident H and D atoms are at \(T \sim 300\) K, chemisorption is improbable unless the formation mechanism is dominated by reactions at defects. TPD of an etched graphite surface irradiated by H atoms at 2000 K was conducted by Zecho et al. (2002). The high temperature of the H atoms allowed them to overcome the 0.2 eV barrier and chemisorb to the surface. The etched surface created terrace edges on the graphite lattice, namely defects. Zecho et al. (2002) found that atoms bond more strongly at the defects. However, there was a minimal change in the recombination of chemisorbed atoms on the formation of terrace edges on the graphite surface, implying that the formation process was dominated by conventional sites on the planar surface. Hydrogen adsorbed on terrace edges was found to desorb primarily in the form of hydrocarbons, rather than molecular hydrogen. However, in dark clouds, the energy of the incident atoms is much lower than in the Zecho et al. (2002) experiment. Therefore, it is still feasible that defects dominate the reaction of hydrogen atoms at low temperatures. In this case, theoretical work based on chemisorption and the Eley–Rideal mechanism, such as that by Takahashi & Uehara (2001), may be more accurate than results from the UCL Cosmic Dust Experiment.

The charge state of a grain is likely to affect surface chemistry (e.g., Caruana & Holt 2010). If the charge on the grain is largely delocalized, then one would not expect there to be much effect on the recombination of two H atoms. If the charge is localized near the H\textsubscript{2} formation site, then it may be harder for the molecule to escape the grain, hence reducing the formation rate.

A more important factor is the dust grain morphology, in particular the porosity of the surface. Both bare and icy grains may exhibit a microporous structure (Greenberg 2002; Williams & Herbst 2002; Williams et al. 2007). Although atoms are mobile on porous grains (Matar et al. 2008) and recombination is efficient (Hornekaer et al. 2003), the nascent hydrogen molecules are found to thermalize in the pores, losing kinetic and internal energy. Therefore, although the H\textsubscript{2} molecule may originally form with rovibrational excitation, subsequent collisions with pore walls may mean that there is no apparent formation pumping of molecules that have escaped the grain surface. Congiu et al. (2009) have shown experimentally that D\textsubscript{2} does not form vibrationally excited on porous surfaces.

The work presented in this paper incorporates our new formation pumping model from the UCL Cosmic Dust Experiment, as well as some theoretical models, such as the work put forward by Takahashi & Uehara (2001). We also include a model in which there is no apparent formation pumping. We compare spectra generated by these different formation pumping models in order to find observational markers to discriminate between formation pumping mechanisms.

### 3. The H\textsubscript{2} Level Distribution Model

We have constructed models to compute the H\textsubscript{2} level distribution expected in a thermally excited gas, based on a radiative transfer code developed to study H\textsubscript{2} formation pumping (Casu 2006). The details of the code are beyond the scope of this paper. Here, we present a summary of the results. The model is based on a two-level formalism, where the levels are the lower and upper states of the H\textsubscript{2} molecule. The transitions between these levels are mediated by collisional and radiative processes. The rate coefficients for these processes are obtained from a detailed analysis of the literature and the results of theoretical calculations. The model includes a variety of physical and chemical processes, such as collisional excitation, radiative de-excitation, and chemical reactions, that can influence the level distribution of H\textsubscript{2}.

#### Table 1

| \(v/J\) | 0 | 1 | 2 | 3 | 4 | 5 | 6 |
|-------|---|---|---|---|---|---|---|
| 0     | 0.0052* | 0.0279 | 0.0048 | 0.0061 | 0.0006 |
| 1     | 0.0052 | 0.0279 | 0.0048 | 0.0061 | 0.0006 |
| 2     | 0.0058 | 0.0276 | 0.0116 | 0.0180 | 0.0016 |
| 3     | 0.0213 | 0.1245 | 0.0245 | 0.0402 | 0.0073 | 0.0056 | 0.0005 |
| 4     | 0.0362 | 0.1907 | 0.0539 | 0.0750 | 0.0108 | 0.0124 | 0.0020 |
| 5     | 0.0135 | 0.0568 | 0.0266 | 0.0293 | 0.0052 | 0.0035 | 0.0011 |
| 6     | 0.0026 | 0.0163 | 0.0057 | 0.0045 | 0.0009 |
| 7     | 0.0021 | 0.0118 | 0.0039 | 0.0070 |

Note. * Rotational populations of \(v = 0\) are taken equal to the populations of \(v = 1\) (see the text).
& Cecchi-Pestellini 2005) and excitation in turbulent diffuse interstellar clouds (Cecchi-Pestellini, Casu & Dalgarno 2005). The approach is similar in some respects to those developed by Sternberg & Dalgarno (1989) and Draine & Bertoldi (1996). However, we do not adopt the cascade efficiency factor formalism (Black & Dalgarno 1976) and solve the full set of statistical equilibrium equations for the first $N = 300$ levels of $H_2$. We describe the depth-dependent $H_2$ photodissociation rates by self-shielding functions (van Dishoeck & Black 1988; Sternberg & Dalgarno 1995), including the prescription for the line overlap given in Draine & Bertoldi (1996). All radiation-induced processes have been computed taking into account dust extinction, which has been assumed to follow the mean galactic interstellar extinction curve (e.g., Fitzpatrick & Massa 2007).

In statistical equilibrium, the $\Lambda$ populations $n_i = (v, J)$, of the $H_2$ levels are solutions to the set of algebraic equations:

$$n_i = \left\{ \sum_{j < i} (A_{ij} + C_{ij} + W_{ij}) + \sum_{j > i} (C_{ij} + W_{ij}) + \beta_i + \zeta + D_i + K^\infty_i \right\}$$

$$= \sum_{j < i} n_j A_{ji} + \sum_{j > i} n_j (C_{ji} + W_{ji}) + K^\infty_i + R n_{H_2} n_1 \delta_i,$$  \hspace{1cm} (1)

where $W_{ij}$ are the excitation rates from the level $i$ to level $j$ via UV pumping to electronically excited states, $A_{ij}$ are the Einstein coefficients for spontaneous radiative decay, $C_{ij}$ are the temperature-dependent collisional rates, $\beta_i$ is the rate of photodissociation out of the level $i$, $D_i$ is the rate of additional destruction processes, such as collisional dissociation and ionization, and $K^\infty_i$ are entry (+) and exit (−) chemical rates. The cosmic-ray destruction rate is denoted by $\zeta$. The last term on the right-hand side of Equation (1) describes the formation of $H_2$ via grain catalysis: $R$ is the formation rate, $n_{H_2}$ is the total volume density of hydrogen, $n_1$ is the volume density of atomic hydrogen, and $\delta_i$ is the fraction of $H_2$ formed on grain surfaces that leaves the grain in level $i$. The highest lying state is $(v, J) = (3, 27)$ at about 52,000 K above the ground state. The level populations are subject to the normalization conditions

$$\sum_{i,j} n_{ij} = n_{H_2},$$

where $n_{H_2}$ is the number density of hydrogen molecules.

The radiative transfer code includes inelastic collisions with $H$, $He$, and ortho- and para-$H_2$, with fully quantum mechanical calculations of collisional rates given in studies by Flower (1998), Flower & Roueff (1998a, 1998b), Flower et al. (1998), and Le Bourlot et al. (1999). For levels where quantum calculations are not available, the extrapolation scheme for the $H$–$H_2$ rate collisions provided by Le Bourlot and co-workers in their code for photon-dominated regions (PDRs) has been adopted (J. Le Bourlot 2005, private communication). For all other collisional partners when quantum calculations are lacking, the collision scheme put forward by Tinée et al. (1997) has been employed. For models with temperatures larger than 30 K, we have incorporated three rate coefficients for ortho–para conversions provided by Sun & Dalgarno (1994). Energy levels, radiative decay rates, and dissociation probabilities for electronic transitions have been published by Abgrall et al. (1992), Abgrall et al. (1993), Abgrall et al. (1993b), and Abgrall et al. (2000). Extra data, covering levels up to $J = 25$, were kindly provided by H. J. Abgrall (2000, private communication). Quadrupole radiative decays and energies of rovibrational levels of the ground electronic state were taken from Wolniewicz et al. (1998).

The $H_2$ formation rate is more fully described by moment equations (Le Petit et al. 2009), rather than by rate equations using the expression $R n_{H_2} n_1 \delta_i$. This is because small grain sizes and low atom fluxes are subject to large fluctuations, and thus calculating the $H_2$ formation rate requires stochastic methods. However, Le Petit et al. (2009) find that the moment equation results agree with the rate equation results in a wide range of conditions, except for dust grains at temperatures larger than 18 K, in which case the rate equations overestimate the $H_2$ formation rate. For dark clouds, as investigated in this paper, where dust temperature are $\sim 10$ K throughout the cloud, the $H_2$ formation rate can be adequately described using the standard rate equation term assumed in Equation (1). Of course, if the radiation environment differs substantially from the standard interstellar conditions, dust temperatures may be noticeably larger than 20 K (see Section 4).

In the present study, for all formation pumping models, except the one presented in Section 2, the relative (normalized) populations of the rovibrational states are given by

$$\delta_{vJ} = C g_N f_1(v, J) \exp[- f_2(\Delta E_{vJ}, T_f)],$$  \hspace{1cm} (2)

where $C$ is a normalization constant and $\Delta E_{vJ}$ is the energy in K of level $(v, J)$ referred to the ground state. $f_1$ and $f_2$ are shape functions depending on the specific formation model. We consider the following $H_2$ formation pumping models:

(i) the formation pumping model described in Section 2, where $\delta_{vJ}$ is taken directly from extrapolation of HD experiments (see Table 1);
(ii) the acquired internal energy, $E_i$ is statistically distributed among the energy levels, $f_1 = 2J + 1$ and $f_2 = \Delta E_{vJ}/T_f$; by setting the formation temperature to $T_f = 9000$ K the model proposed by Black & Dalgarno (1976) is recovered

$$\sum_{vJ} n_{H_2} \times (2J + 1) \Delta E_{vJ} \exp(- \Delta E_{vJ}/T_f) \sim 1.5 \text{ eV}/k_B,$$  \hspace{1cm} (3)

with $k_B$ being the Boltzmann constant;
(iii) to enhance the populations of high $v$ states with respect to high $J$ states, we set $f_1 = v + 1$; this class of formation models with $T_f = 50,000$ K provides the pumping profile suggested by Draine & Bertoldi (1996);
(iv) the three rovibrational population distributions for $H_2$ newly formed on carbonaceous dust $(iv-c)$, silicate dust $(iv-s)$, and icy mantles $(iv-i)$ given by Takahashi & Uehara (2001), model A; the functions $f_1$ and $f_2$ are taken from Takahashi & Uehara (2001);
(v) the same as in (iv) but for Takahashi & Uehara (2001) model B;
(vi) a minimal $H_2$ formation pumping model which limits the rovibrational distribution to the lowest possible levels $(v, J) = (0, 0)$ and $(0, 1)$ in the ratio 1:3; $f_1 = f_2 = 0$ except for $(v, J) = (0, 0)$ and $(0, 1)$ when $f_1 = 1$; this represents the “no formation pumping” case. If nascent $H_2$ molecules in dark clouds thermalize with the dust grain pores or the icy mantle, as put forward by Congiu et al. (2009), then no formation pumping would be detected.

4. $H_2$ IR EMISSION FROM DARK CLOUDS

The cloud is assumed to be a plane–parallel slab of constant density, $n_H$. The cloud is two-sided illuminated by an isotropically incident UV radiation field. The field intensity is assumed to be the UV field scaling parameter, $\chi$, times the Draine (1978) estimate of the mean interstellar radiation field as reported in Sternberg & Dalgarno (1989). The attenuation of the field due to
dust extinction is computed using the analytical solution to the transport equation in plane–parallel geometry given in Flannery et al. (1980). The H/H\textsubscript{2} ratio calculations as a function of depth have been supplemented with the time- and depth-dependent gas-grain UCL\_CHEM chemical model (Viti et al. 2004). In addition, we use the UCL\_PDR code (Bell et al. 2006) in order to get the cloud thermal profile. We find that gas temperatures are higher than \sim 10 K only at the very edge of dark clouds. However, in the case of translucent clouds, or non-standard illumination (\chi > 1), gas temperatures may be significantly larger than 10 K throughout the cloud.

We perform calculations for translucent and dark clouds of number densities \( n_\text{H} = 10^3–10^6 \text{ cm}^{-3} \), cosmic-ray ionization rate \( \xi = 3 \times 10^{-17} \text{ s}^{-1} \), and column densities \( N_\text{H} = 4.8 \times 10^{21}–1.6 \times 10^{23} \text{ cm}^{-2} \), corresponding to visual integrated magnitudes \( A_V = 3–100 \) (e.g., Snow & McCall 2006). Dark clouds were chosen following the suggestion by Dudley & Williams (1993) and Tiné et al. (2003) that quiescent, dense clouds with no UV pumping are the regions of the ISM best suited to detect formation pumping. We extend the calculations to clouds with moderate extinctions in order to get larger formation pumping rates, although contamination from radiative pumping may be substantial (as is actually the case). For such clouds, the UCL\_PDR code in the density range \( 10^3–10^6 \text{ cm}^{-3} \) provides thermal profiles in which the “10 K edge” is reached at \( A_V = 1–2.5 \text{ mag} \), measured from the external boundary of the cloud. For \( \chi > 100 \), the UCL\_PDR code also finds that dust temperatures are larger than 20 K. In that case, the use of rate equations for \text{H}_2 formation may not be accurate (Le Petit et al. 2009).

In Figure 2, we compare the results for the six formation pumping profiles, described in Section 3, for the case of dark clouds of hydrogen density \( n_\text{H} = 10^6 \text{ cm}^{-3} \), \( R = 3 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1} \), \( \xi = 3 \times 10^{-17} \text{ s}^{-1} \), standard UV field (\( \chi = 1 \)), and integrated visual extinction \( A_V = 100 \text{ mag} \), hereafter called the reference cloud model (RCM). The emissivities roughly scale with the simulated instrumental resolution. We assume an FWHM of \( 5 \times 10^{-3} \mu\text{m} \), approximately corresponding to the instrument resolution of echelle spectrometers used by current ground-based telescopes such as the Phoenix instrument on the Gemini telescope, which has a resolution of 50,000–80,000 for near-IR wavelengths 1–5 \( \mu\text{m} \) (Hinkle et al. 2000). All of these pumping models provide distinct spectral features. Therefore, in principle, astronomical observations could be used to identify the actual formation pumping mechanism taking place in the ISM. However, a common pattern is apparent in all the generated spectra in Figure 2. As the adopted pumping mechanisms result in quite different \text{H}_2 level excitation rates, the underlying common level distribution must be generated by some global ambient mechanism, such as thermal pumping. However, collisional excitation cannot be significant as the RCM kinetic temperature is approximately 10 K in most parts of the cloud. These spectra are the result of radiative transfer throughout the whole cloud, enfolding both translucent and dense cloud regimes. Therefore, the features present in the IR spectra might originate via UV pumping close to the edge of the cloud, in a region in which all the hydrogen is not yet in the molecular form. In the bottom right panel of Figure 2, we show the IR spectrum generated by model (vi), in which formation pumping is not active, but nevertheless a rich spectrum is present: radiative pumping in the translucent regime tends to dominate the emission even at large extinctions. This interpretation is supported by the spectrum shown in Figure 3, derived for a cloud model with the same physical parameters as the RCM, but with visual extinction \( A_V = 5 \text{ mag} \). The increase of the emission in the lower \( A_V \) cloud model with respect to the RCM is mainly due to residual UV radiation coming from the opposite edge of the cloud. In Table 2, we report wavelength-integrated emission intensities produced in different cloud models, including the spectra displayed in Figures 2 and 3. Since the residual field scales with the size of the cloud (in plane–parallel clouds of constant density), an increase in \( A_V \) produces a decrease in the emitted integrated intensity, when the main pumping mechanism is radiative. We also note that in the RCM, depending on the formation model, \text{H}_2 formation pumping produces an IR excess of about 20%–40% with respect to the UV-pumped IR background.

To highlight spectral features arising from specific \text{H}_2 formation pumping profiles, we show in Figure 4 the residual spectra computed for the RCM after subtraction of the “background” UV pumping contribution, i.e., the spectrum arising in model (vi) (right bottom panel of Figure 2). Since radiative transfer couples different parts of the cloud, residual spectra may provide an indication of the formation pumping effect, but in general they cannot be considered as an “exact” measure of the formation pumping contribution to line excitation. The most intense residual emission lines produced by the formation pumping are reported for each model in Table 3. Model (i) shares some features with model (iii) only. All the other formation pumping present several common features. Our proposed formation pumping model produces spectra where the highest vibrational level is \( v = 4 \), with no lines from high rotational states in the 4–5 \( \mu\text{m} \) region. In model (ii) (Black & Dalgarno 1976), high rotational levels are pumped, as expected, with the highest being \( J = 16 \) (at an intensity level of \( 1 \times 10^{-4} \text{ erg cm}^{-2} \text{ sr}^{-1} \mu\text{m}^{-1} \)). Although presenting the highest integrated intensities, models (ii) (Black & Dalgarno 1976) and (iii) (Draine & Bertoldi 1996) do not show very prominent spectral features, because of the wide dispersion of the internal energy over a large number of vibrational states. Models (iv) and (v) (Takahashi & Uehara 2001) show high rotational states, as well as a combination of moderately high \( v \) and \( J \), such as the \((v, J) = (3, 9)\) state. These models provide quite different spectral patterns, with the former showing brighter lines, while the latter exhibits a richer spectrum. The most intense transition for model (i) is \((4 - 2) \text{ O}(3)\), whereas the \((1 - 0) \text{ S}(7)\) line is strongest for all other models. In Table 3, we present emission lines computed for model (vi). Since, in this model, formation pumping is suppressed, spectral features arise from radiative and collisional pumping close to the edge of the cloud. Transitions involving low rotational states \((J \leq 5)\) show a systematic mixing of internal and environmental pumping mechanisms. As a consequence, our formation pumping model, which predicts little rotational excitation, appears to produce an emission spectrum contaminated by external factors. This contamination does not occur for cases where the emission is dominated by transitions from high rotational states, such as the \((1 - 0) \text{ S}(7)\) line in the Black & Dalgarno (1976) model.

In Figures 5 and 6, we show the volume emissivities of the \((4 - 2) \text{ O}(3)\) and \((1 - 0) \text{ S}(7)\) lines as functions of the optical thickness within the cloud. The \((4 - 2) \text{ O}(3)\) transition has been computed for models (i) and (vi) in the translucent and dense cloud regimes, while the \((1 - 0) \text{ S}(7)\) transition has been computed for models (ii)–(v). In these figures, we also present the most important relative contributions to the population of the upper state of the transitions due to the included excitation.
mechanisms, see Equation (1); these mechanisms are UV pumping by fluorescent cascade from excited electronic states, IR cascade within the ground state, thermal collisions and excitation due to H\textsubscript{2} formation on dust grains. The excitation of the (4 − 2) O(3) line is driven by radiation close to the edge of the cloud, but is dominated by formation pumping in the cloud interior. Since collisional rates scale with density, thermal collisions contribute to the line excitation in response to the very high density adopted for the RCM. In the case of the low-density translucent cloud model, thermal excitation is negligible. In model (vi), line emission is essentially the same as for model (i) until the external UV radiation density declines sharply for A\textsubscript{V} \gtrsim 1\ mag. No line excitation is produced because formation pumping is suppressed in model (vi). For the transition (1 − 0) S(7) in models (ii)–(v), the situation is different. The line excitation at large visual depth is almost completely dominated by the IR cascade (\sim 90\%) rather
than by direct excitation from the formation process (~10%). However, since UV pumping is not effective for large $A_V$, the high energy levels must be populated by formation pumping. The IR cascade then populates ($v, J$) = (1, 9) and lower energy levels. This is directly dependent on the distribution of the internal energy over a large number of rovibrational levels, as occurs in models (ii)–(v). In contrast, only a small number of rovibrational levels are populated in model (i). Therefore, the excitation of the (1–0) S(7) line is essentially driven by formation pumping. This conclusion is supported by the lack of significant emission at the corresponding wavelength in model (vi) (see Table 3).

We now discuss the dependency of the IR spectra on cloud parameters. In Table 4, we present line intensities for 4 – 2 O(3), 1 – 0 S(7), and 1 – 0 Q(1) transitions using the set of cloud models defined in Table 2. The physical conditions of such models cover a wide portion of the parameter space. In Table 5, we show the excitation and de-excitation rates for the upper levels of the 4 – 2 O(3) and 1 – 0 S(7) transitions, for selected positions within the cloud. We find the following.

1. The integrated spectrum intensity increases almost linearly with $\chi$, as expected if the excitation is dominated by the emission in the translucent regime (see Table 2). The IR excess provided by formation pumping decreases with increasing UV radiation density, e.g., in the case of model (i) the excess is 20% when $\chi = 1$, while it is less than 4% when $\chi = 1000$.

2. Integrated intensities decrease with increasing $A_V$ (and hydrogen column density): this is a direct consequence of the fact that, in a double-sided-illuminated cloud, the boundaries may be reached by residual radiation coming from the opposite edge. Integrated intensities do not decrease when the gas density is $n_H = 10^3$ cm$^{-3}$: in such a case, since only a partial conversion of hydrogen from atomic to molecular form takes place, lines pumped by formation get significantly brighter, even if the overall IR emission does not increase.

3. Line spectra vary marginally with increasing number and column densities as soon as hydrogen is almost totally converted to the molecular form. In clouds where partial H$_2$ conversion occurs, line intensities are larger than in dense clouds where emission paths are considerably longer.

4. The strength of a line increases steadily, although not linearly, with kinetic temperature, because as the temperature rises, more collisional pumping occurs, although the shape of the spectrum does not greatly alter. In general, when kinetic temperature increases over 100 K in a substantial fraction of the cloud, there is a sharp rise in the strength of

Table 3

| Wavelength ($\mu$m) | Transition | Residual Intensity$^a$ | Intensity $^{(10^{-4}$ erg s$^{-1}$ cm$^{-2}$ sr$^{-1}$ $\mu$m$^{-1}$)) | (i) | (ii) | (iii) | (iv – c) | (v – c) | (vi) |
|-------------------|------------|------------------------|----------------------------------------------------------------|-----|-----|-----|------|------|-----|
| 0.90274           | (4–1) Q(1) | 1.5                    | 1.8                                                           | 3.1  | 2.0 |
| 1.06360           | (2–0) S(7) | 1.8                    | 2.0                                                           | 4.3  | 1.2 |
| 1.11988           | (3–1) S(9) | 2.0                    | 2.3                                                           | 4.3  | 1.2 |
| 1.18508           | (3–1) S(3) | 1.3                    | 1.4                                                           |      |     |
| 1.23235           | (3–1) S(1) | 2.7                    | 1.7                                                           | 6.0  |     |
| 1.31342           | (3–1) Q(1) | 3.3                    | 1.1                                                           | 6.8  |     |
| 1.33475           | (2–0) O(3) | 4.1                    | 1.3                                                           | 8.2  |     |
| 1.40617           | (2–0) Q(13)| 1.1                    | 12.4                                                          |      |     |
| 1.50913           | (4–2) O(3) | 7.4                    | 2.0                                                           | 12.4 |     |
| 1.71389           | (1–0) S(8) | 1.7                    | 1.1                                                           | 2.8  | 1.2 |
| 1.74707           | (1–0) S(7) | 6.5                    | 4.5                                                           | 10.7 | 6.1 |
| 1.83479           | (1–0) S(5) | 3.8                    | 3.8                                                           | 4.6  | 4.8 |
| 1.94392           | (2–1) S(5) | 1.1                    | 1.6                                                           | 1.6  | 0.3 |
| 2.15318           | (2–1) S(2) | 1.2                    | 1.0                                                           | 10.0 |     |
| 2.40524           | (1–0) Q(1) | 4.7                    | 1.9                                                           | 11.2 |     |
| 2.54981           | (2–1) Q(1) | 2.3                    | 4.6                                                           |      |     |
| 2.78490           | (2–1) O(2) | 1.3                    | 14.9                                                          |      |     |
| 2.80027           | (2–1) Q(11)| 1.3                   | 12.6                                                          |      |     |
| 2.97273           | (2–1) O(3) | 6.2                    | 2.0                                                           |      |     |
| 3.54591           | (0–0) S(16)| 1.2                   | 1.2                                                           |      |     |
| 3.72256           | (0–0) S(14)| 2.2                   | 2.2                                                           |      |     |
| 3.83849           | (1–1) S(15)| 1.2                   | 1.2                                                           |      |     |
| 3.84413           | (0–0) S(13)| 1.2                   | 1.2                                                           |      |     |
| 4.07916           | (2–2) S(15)| 1.3                   | 1.3                                                           |      |     |
| 4.17881           | (0–0) S(11)| 2.4                   | 2.1                                                           | 1.3  |     |
| 4.22152           | (1–1) S(12)| 1.2                   | 1.2                                                           |      |     |
| 4.41439           | (1–1) S(11)| 2.2                   | 1.1                                                           | 3.0  | 1.6 |
| 4.95163           | (1–1) S(9) | 3.3                   | 5.6                                                           | 2.6  |     |

Note. $^a$ peak line intensities larger than $1 \times 10^{-4}$ erg s$^{-1}$ cm$^{-2}$ sr$^{-1}$ $\mu$m$^{-1}$.
Figure 4. Residual IR spectra. The strongest spectral lines are identified. Different models are indicated as in Figure 2.
the \(1 - 0\) Q(1) line, due to thermal excitation of H\(_2\) to the \((v, J) = (1, 1)\) level.

5. For both levels \((v, J) = (1, 9)\) and \((4, 1)\) in any position within the RCM, the major exit channel is radiative de-excitation; the major entry channel is direct formation pumping for level \((v, J) = (4, 1)\), and IR cascade from upper levels for \((v, J) = (1, 9)\). Since both UV fluorescence and thermal collisions are negligible in most parts of the cloud, the pumping of high rovibrational states is due to H\(_2\) formation on dust grains.

6. As there is uncertainty in the population of the \(v = 0\) levels (see Section 2.1), H\(_2\) spectra have been generated for a distribution where the \(v = 0\) levels are twice as populated as the \(v = 1\) levels and for a distribution where the \(v = 0\) levels are half as populated as the \(v = 1\) levels. These changes make only a minimal difference to line strengths, with spectra similar to within 4\%.

Finally, in Figure 7, we show the residual emission spectrum of a standard translucent cloud \((n_H = 10^5 \text{ cm}^{-3}, A_V = 5 \text{ mag})\), all other parameters are as for the RCM) for the case of model (i). It appears that in a cloud of moderate density and extinction, the intensity of the emitted spectrum is 3–4 times more intense than in the case of the RCM, in which the hydrogen column density is 20 times larger. The increase in line strength is more evident for lines produced during H\(_2\) formation. This reflects the much larger abundance of atomic hydrogen (by about a factor of 1000) in the lower density cloud. The comparison with the RCM case also shows that the very long emission path inside a dense cloud produces only a marginal increase in the line intensities, since the abundances of the upper levels in the emitting transitions fall abruptly as soon as H\(_2\) formation saturates.

5. DISCUSSION AND CONCLUSIONS

In this work, we investigate the effects of formation pumping in IR H\(_2\) emission spectra with a new formation pumping model (Table 1). We construct radiative transfer and chemical models for H\(_2\) newly formed on dust grains. By using realistic space-dependent cloud models, we find that UV radiative...
Figure 6. 1–0 S(7) line emissivities (cm\(^{-3}\) s\(^{-1}\) sr\(^{-1}\)) as functions of the optical thickness (in mag) computed for models (ii), (iii), (iv – c), and (v – c) (solid lines), in the case of RCM. The relative contributions to the population of the upper state of the transition \((v, J) = (1, 9)\) are: formation pumping (dotted line), IR rovibrational cascade within the ground electronic state (dashed line), UV fluorescent cascade from excited electronic levels (dot-dashed line), and thermal collisions (triple-dot-dashed line).

Figure 7. Residual IR spectrum for a translucent cloud with gas density \(n_H = 10^3\) cm\(^{-3}\) and \(A_V = 5\) mag. All other parameters are as for RCM.

Surprisingly, spectra show a very modest increase with both volume and column densities. IR emission is expected to scale with the square of volume density and linearly with column density, via the formation rate and the path along the line of sight. However, deep within a cloud \((A_V \gtrsim 2.5\) mag) an almost total conversion of hydrogen from atomic to molecular form occurs. Thus, the emissivity produced in the inner zone of a cloud is “lost” within the contribution originating in the transition zone, in which \(H_2\) abundances are still comparable to those of atomic hydrogen. In other words, the bulk of the emission is coming from the “translucent” regime close to the edge of a cloud.

This can be easily understood considering a simple two-level model representing an emission line \(u \rightarrow l\) arising during the \(H_2\) formation process within a homogeneous cloud. In such a representation, the line emissivity is given by

\[
\epsilon = \frac{hc}{4\pi\lambda} A_{ul} n_u \phi_l \quad \text{with} \quad A_{ul} n_u \sim R n_H n_1 \delta_u, \tag{4}
\]

(see Table 5), while the brightness is obtained by integration of Equation (4) along the line of sight \(\Delta L\):

\[
\delta I_\lambda \sim \frac{hc}{4\pi\lambda} R n_H^2 n_1 x_1 \delta_u \phi_l \Delta L. \tag{5}
\]

In Equations (4) and (5), \(\phi_l\) is the assumed line profile, \(n_u\) is the population of the upper level of the transition, and \(x_1\) pumping dominates the emission even in clouds with very high visual extinction. After eliminating radiative pumping, we obtain residual IR spectra due to formation pumping. When cloud kinetic temperatures rise over 100 K, thermally excited rovibrational levels of the \(v = 1\) manifold may contribute to the overall IR spectrum.
is the fractional abundance of atomic hydrogen. The intensity ratio between emissions originating from dense and translucent regions in the cloud then results

\[ \frac{\delta I^D_T}{\delta I^T_T} = \frac{x^D_T N^D_H}{x^T_T N^T_H} \lesssim 10^{-3} \times \frac{N^D_H}{N^T_H}. \tag{6} \]

We get \( \delta I^D_T \sim \delta I^T_T \) when \( N^D_H \sim 1000 \times N^T_H \). Since in the RCM, \( N^D_H/N^T_H \sim 20 \), we finally obtain \( \delta I^D_T \lesssim 2\% \delta I^T_T \). Thus, emission from the translucent outer regions of a cloud dominates the spectral line intensity, with only a small contribution from the dense central regions of the dark cloud. Consequently, models of formation pumping that are rotationally cool, such as the one put forward in this work, are heavily contaminated by pumping processes arising from nebular physical conditions.

It is possible that only lines from high rotational levels can be identified observationally as being due to formation pumping. Unfortunately, most of the models proposed in the literature have common features (see Table 3) and, in general, it appears difficult to discriminate between them. In contrast, our new formation pumping model produces a spectrum differing significantly from the line patterns of all the other proposed models, and may provide an unambiguous signature for detection, but only from regions not contaminated by UV radiation. In addition, the observation of H$_2$ molecules newly formed on dust grains appears to be currently very difficult. The peak intensity of the spectral lines is of the order of 0.001 erg s$^{-1}$ cm$^{-2}$ sr$^{-1}$ $\mu$m$^{-1}$ (see Figure 2), or \( I_\lambda \sim 1 \times 10^{-16} \) W m$^{-2}$ arcsec$^{-2}$ $\mu$m$^{-1}$. Using a resolution \( R = \lambda/\Delta\lambda = 37,000 \) (taken from UKIRT webpages\(^3\)), we obtain an integrated brightness at 2 $\mu$m of \( I \sim 1.2 \times 10^{-21} \) W m$^{-2}$ arcsec$^{-2}$. Hence, using the UKIRT 1-pixel slit, which is 0.609 arcsec wide, we obtain a flux of \( F \sim 4.5 \times 10^{-22} \) W m$^{-2}$ (for an extended source). This flux is much lower in comparison to the 3 $\sigma$ 30 minute sensitivity per pixel obtained with the echelle grating, which has values 8 $\times$ 10$^{-20}$ W m$^{-2}$ at 1.6 $\mu$m and 6 $\times$ 10$^{-20}$ W m$^{-2}$ at 2.2 $\mu$m. As a consequence, dark clouds are not a good place to look for signatures of H$_2$ formation, since an increase in the emission path does not correspond to a significant increase in the intensity of the spectrum.

Therefore, H$_2$ formation pumping may be undetectable in those regions in which molecular hydrogen is not destroyed at a fairly fast rate. Thus, within the current regime of instrument sensitivity, the non-detections of H$_2$ IR emission in dense clouds reported by Tiné et al. (2003) and Congiu et al. (2009) need not to be explained by the thermalization of nascent H$_2$ molecules on the surface of dust grains, as suggested by Congiu et al. (2009). In dense PDRs, UV radiation maintains a substantial level of atomic hydrogen in the gas. However, the radiation also causes excitation of H$_2$ to the Lyman and Werner bands, inducing IR fluorescence to further complicate the emission process. Much

\[^3\]http://www.jach.hawaii.edu/UKIRT/instruments/cgs4/optical/resolution.html
respectively (Dalgarno et al. 1999). The excitation rate to the
excited electronic states is thus
\\\[ \text{discrete interactions only provide excitations in the H}_2 \text{ vibrational ladder up to } v = 2 \] (Dalgarno et al. 1999). The radiative
decays of the electronically excited H and H$_2$ produce FUV photons, H$_2$ Lyman–Werner photons, and H Ly$_\alpha$ photons. We can estimate the impact of photoelectron-induced UV radiation in the following way: assuming photoelectrons of mean energy 30 eV (as in Tiné et al. 1997), the numbers of excitations to the states $B^2 \Sigma_u^+$ and $C^3 \Pi_u$, including the contribution of cascading from higher singlet states, are approximately 0.6 and 0.4, respectively (Dalgarno et al. 1999). The excitation rate to the excited electronic states is thus $\sim \chi_\lambda$, where $\chi_\lambda$ is the total X-ray ionization rate. The radiative excitation of Lyman and Werner bands is roughly $5 \times 10^{-10} \chi \lambda$ s$^{-1}$ (Draine & Bertoldi 1996). We obtain the equivalent UV field scaling factor by means of the relation $\chi = \chi_\lambda/5 \times 10^{-10}$. Thus, the most prominent feature in the IR spectrum generated using our formation pumping model, namely the transition $4 \rightarrow 2$ O(3), would be minimally affected by X-rays, as long as the ionization rate is $\chi_\lambda \ll 5 \times 10^{-10}$ s$^{-1}$.

In Figure 8, we report the intensity of the line $4 \rightarrow 2$ O(3) as a function of the H$_2$ ionization rate in the RCM. It is evident that the transition $4 \rightarrow 2$ O(3) might be observed if the H$_2$ ionization rate is $\chi_\lambda \gtrsim 1 \times 10^{-14}$ s$^{-1}$, in agreement with Le Bourlot et al. (1995). In this case, since the line intensity scales approximately with the ionization rate, the line would be largely dominated by formation pumping rather than radiative pumping. The crucial point is that XDRs may maintain large ionization rates up to $1 \text{ keV}$ (Cecchi-Pestellini et al. 2009).

In conclusion, we model H$_2$ formation pumping in standard dense clouds, taking into account the H/H$_2$ transition zone. The
REFERENCES

Abgrall, H. J., Le Bourlot, J., Pineau de Forêts, G., Roueff, E., Flower, D. R., & Heck, L. 1992, A&A, 253, 525
Abgrall, H. J., Roueff, E., & Drira, I. 2000, A&AS, 2000, 141, 297
Abgrall, H. J., Roueff, E., Launay, F., Roncin, J. Y., & Subtil, J. L. 1993a, A&AS, 101, 273
Abgrall, H. J., Roueff, E., Launay, F., Roncin, J. Y., & Subtil, J. L. 1993b, A&AS, 101, 323
Amiaud, L., Dulieu, F., Fillion, J. H., Momeni, A., & Lemaire, J. L. 2007, J. Chem. Phys., 127, 144709
Bell, T. A., Roueff, E., Viti, S., & Williams, D. A. 2006, MNRAS, 371, 1865
Black, J. H., & Dalgarno, A. 1976, ApJ, 203, 132
Caranana, D. J., & Holt, K. B. 2010, Phys. Chem. Chem. Phys., 12, 3072
Casu, S., & Cecchi-Pestellini, C. 2005, J. Phys. Conf. Ser., 6, 191
Cecchi-Pestellini, C., Casu, S., & Dalgarno, A. 2005, MNRAS, 364, 1309
Cecchi-Pestellini, C., Ciaravella, A., Micela, G., & Penz, T. 2009, A&A, 496, 863
Congiu, E., Matar, E., Kristensen, L. E., Dulieu, F., & Lemaire, J. L. 2009, MNRAS, 397, L96
Creighan, S. C., Perry, J. S.A., & Price, S. D. 2006, J. Chem. Phys., 124, 114701
Dalgarno, A., Yan, M., & Liu, W. 1999, ApJS, 125, 237
Draine, B. T. 1978, ApJS, 36, 595
Draine, B. T., & Bertoldi, F. 1996, ApJ, 468, 269
Duley, W. W., & Williams, D. A. 1986, MNRAS, 223, 177
Duley, W. W., & Williams, D. A. 1993, MNRAS, 260, 37
Farebrother, A. J., Meijer, A., Clary, D. C., & Fisher, A. J. 2000, Chem. Phys. Lett., 319, 303
Fitzpatrick, E. L., & Massa, D. 2007, ApJ, 663, 320
Flannery, B. P., Roberge, W., & Rybicki, G. B. 1980, ApJ, 236, 598
Flower, D. R. 1998, MNRAS, 297, 334
Flower, D. R., & Roueff, E. 1998a, J. Phys. B: At. Mol. Opt. Phys., 31, L955
Flower, D. R., & Roueff, E. 1998b, J. Phys. B: At. Mol. Opt. Phys., 31, 2935
Flower, D. R., Roueff, E., & Zeippen, C. J. 1998, J. Phys. B: At. Mol. Opt. Phys., 31, 1105
Gough, S., Schermann, C., Pichou, F., Landau, M., Cadez, I., & Hall, R. I. 1996, A&A, 305, 687
Gould, R. J., & Salpeter, E. E. 1963, ApJ, 138, 393
Grenberg, J. M. 2002, Surf. Sci., 500, 793
Hinkle, K., Joyce, R., Sharp, N., & Valenti, J. A. 2000, Proc. SPIE, 4008, 720
Hollenbach, D., & Salpeter, E. E. 1970, J. Chem. Phys., 53, 79
Hornekaer, L., Bourrichter, A., Petrunin, V. V., Field, D., & Luntz, A. C. 2003, Science, 302, 1943
Islam, F., Latimer, E. R., & Price, S. D. 2007, J. Chem. Phys., 127, 064701
Latimer, E. R., Islam, F., & Price, S. D. 2008, Chem. Phys. Lett., 455, 174
Le Bourlot, J., Pineau de Forêts, G., & Flower, D. R. 1999, MNRAS, 305, 802
Le Bourlot, J., Pineau de Forêts, G., Roueff, E., Dalgarno, A., & Gredel, R. 1995, ApJ, 449, 178
Le Petit, F., Barzel, B., Biham, O., Roueff, E., & Le Bourlot, J. 2009, A&A, 505, 1153
Martínazzo, R., & Tantardini, G. F. 2006, J. Chem. Phys., 124, 124703
Matar, E., Congiu, E., Dulieu, F., Momeni, A., & Lemaire, J. L. 2008, A&A, 492, L17
Meijer, A., Farebrother, A. C., Clary, D. C., & Fisher, A. J. 2001, J. Phys. Chem. A, 105, 2173
Parneix, P., & Brechignac, P. 1998, A&A, 334, 363
Perry, J. S. A., & Price, S. D. 2003, A&SS, 285, 769
Roberts, J. F., Rawlings, J. M. C., Viti, S., & Williams, D. A. 2007, MNRAS, 382, 733
Sizun, M., Bachelier, D., Aguillón, F., & Sidis, V. 2010, Chem. Phys. Lett., 498, 32
Snow, T. P., & McCall, B. J. 2006, ARA&A, 44, 367
Sternberg, A., & Dalgarno, A. 1989, ApJ, 338, 197
Sternberg, A., & Dalgarno, A. 1995, ApJS, 99, 565
Sun, Y., & Dalgarno, A. 1994, ApJ, 427, 1053
Takahashi, J. 2001, ApJ, 561, 254
Takahashi, J., Masuda, K., & Nagaoka, M. 1999, ApJ, 520, 724
Takahashi, J., & Uehara, H. 2001, ApJ, 561, 843
Tiné, S., Lepp, S., Gredel, R., & Dalgarno, A. 1997, ApJ, 481, 282
Tiné, S., Williams, D. A., Clary, D. C., Farebrother, A. J., Fisher, A. J., Meijer, A., Rawlings, J. M. C., & Davis, C. J. 2003, A&SS, 288, 377
van Dishoeck, E. F., & Black, J. H. 1988, ApJ, 334, 771
Vidal, G., Roser, J. E., Ling, L., Congiu, E., Manico, G., & Pirrarello, V. 2006, Faraday Discuss., 133, 125
Vidal, G., Roser, J. E., Manico, G., & Pirrarello, V. 2004, J. Geophys. Res. (Planets), 109, 7
Viti, S., Collings, M. P., Dever, J. W., McCoustra, M. R. S., & Williams, D. A. 2004, MNRAS, 354, 1141
Williams, D. A., Brown, W. A., Price, S. D., Rawlings, J. M. C., & Viti, S. 2007, Astron. Geophys., 48, 25
Williams, D. A., & Herbst, E. 2002, Surf. Sci., 500, 823
Wolniewicz, L., Simbotin, I., & Dalgarno, A. 1998, ApJS, 115, 293
Zech, T., Guttler, A., Sha, X. W., Jackson, B., & Kuppers, J. 2002, Chem. Phys., 117, 8486

model, which includes recent laboratory data on H₂ formation, as well as the effects of the interstellar UV field, predicts the populations of gas-phase H₂ molecules and their IR emission spectra. Calculations suggest that some vibrationally excited states of H₂ might be detectable toward lines of sight where significant destruction of H₂ occurs, such as X-ray sources. These results also provide a possible explanation of the lack of detection to date of H₂ formation pumping in dark clouds.

C.C.P., S.V., and S.C. thank the Royal Society for funding an exchange programme between UCL and Cagliari Observatory. We also thank the anonymous referee for helpful comments and suggestions that improved the clarity of the paper.