Rapid Ortho-to-para Nuclear Spin Conversion of H₂ on a Silicate Dust Surface

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Abstract

The H₂ molecule has two nuclear spin isomers, the so-called ortho and para isomers. Nuclear spin conversion (NSC) between these states is forbidden in the gas phase. The energy difference between the lowest ortho and para states is as large as 14.7 meV, corresponding to ~170 K. Therefore, each state of H₂ differs significantly in its chemistry and macroscopic gas dynamics; thus, the ortho-to-para abundance ratio (OPR) of H₂ has significant impacts on various astronomical phenomena. For a long time, the OPR of nascent H₂ upon formation on dust grains has been assumed to have a statistical value of 3 and to gradually equilibrate in the gas phase at the temperature of the condensation. Recently, the NSC of H₂ was experimentally revealed to occur on water ice at very low temperatures and thus incorporated into gas–dust chemical models. However, H₂ molecules should form well before dust grains are coated by water ice. Information about how the OPR of H₂ behaves on bare silicate dust before ice-mantle formation is lacking. Knowing the influence of the OPR of H₂ is desirable, if the OPR changes even on a bare silicate surface within an astronomically meaningful timescale. We report the first laboratory measurements of the NSC of H₂ physisorbed on amorphous silicate (Mg₂SiO₄) at temperatures up to 18 K. The conversion was found to occur very rapidly.

1. Introduction

The H₂ molecule consists of two protons and thus has a total nuclear spin of zero or 1 with multiplicities of singlet and triplet, respectively. According to the Pauli exclusion principle, the nuclear spin states of 1 (ortho) and zero (para) are only coupled with the rotational states of odd and even quantum numbers, respectively. In thermal equilibrium, the ortho-to-para abundance ratio (OPR) is expressed by the ratio of rotational Boltzmann distributions for odd and even rotational numbers with spin degeneracies. At temperatures above approximately 200 K, the OPR almost reaches a statistical value of 3, while at the low-temperature limit, it becomes zero. The energetically lowest ortho state with rotational number \( J = 1 \) lies approximately 14.7 meV above the para state with \( J = 0 \). In the gas phase, radiative transition between these two states is forbidden; thus, nuclear spin conversion (NSC) only occurs via spin exchange reactions with protons or hydrogen atoms. The conversion timescale due to these processes in molecular clouds (MCs) is as slow as approximately \( 10^7 - 10^8 \) yr (Wilgenbus et al. 2000; Flower et al. 2006). Therefore, H₂ molecules in each state can be considered energetically different species. Because of the large energy gap between the ortho and para states, the OPR of H₂ has important astronomical meaning. For example, the OPR affects the gas dynamics of core formation in star-forming regions because the heat capacity of H₂ gas is different between the ortho and para states (Vaytet et al. 2014). Because of the slow conversion between two spin isomers, the OPR of H₂ has been used as a tracer of the age of clouds (Pagani et al. 2013). In cold (~10 K) regions such as an MC, the OPR can control the chemical evolution. One of the most discussed issues is the effect of the OPR on the deuterium fractionation of molecules in the gas phase (Bovino et al. 2017). The ion species H₃⁺ is involved in the formation of various interstellar molecules. Once H₃⁺ is deuterated by an ion–molecule reaction, \( H₃⁺ + HD \rightarrow H₂D⁺ + H₂ \), it works as a dominant deuterium fractionation pathway in MCs. When reactant H₃⁺ and products H₂D⁺ and H₂ are all in the para state, this reaction is exothermic by 230 K. However, if H₂ is in the ortho state, then the exothermicity is significantly reduced, resulting in the occurrence of a reverse process that destroys H₂D⁺ even in MCs.

In contrast to processes in the gas phase, little is known about how the OPR of H₂ behaves on dust grains. It has been widely accepted that H₂ predominantly forms via H–H recombination on the surface of dust grains (Wakelam et al. 2017). Furthermore, H₂ molecules in the gas phase inevitably collide and interact with dust grains. Nevertheless, processes on dust surfaces concerning the OPR of H₂ remained unclear for a long time because of the difficulties in both experimental and theoretical approaches. Recently, several experiments finally shed light on the behavior of the H₂ OPR on ice surfaces (Sugimoto & Fukutani 2011; Ueta et al. 2016). The OPR of nascent H₂ formed by H–H recombination was revealed to be almost 3, and NSC can occur on water ice within approximately \( 10^7 \) s, depending on the temperature (Watanabe et al. 2010; Ueta et al. 2016). These experimental findings have now been incorporated into gas–dust chemical models (Bovino et al. 2017; Furuya et al. 2019). However, H₂ formation should be activated and equilibrate on bare silicate or carbonaceous dust well before ice-mantle formation. Therefore, knowing whether NSC occurs to change the OPR of H₂ on these surfaces is highly desirable.

2. Experiment

The experiments were performed in an ultrahigh vacuum chamber (~\( 10^{-8} \) Pa) with a doubly differentially pumped molecular beam source. An amorphous silicate film was deposited on an aluminum substrate by pulsed laser ablation of an Mg₂SiO₄ target in situ; the preparation and characterization of the film are described in Appendix A.1. The substrate
was located at the center of the main chamber and could be cooled by a closed-cycle helium refrigerator. The NSC of H$_2$ on the Mg$_2$SiO$_4$ surface was investigated with a combination of temperature programmed desorption (TPD) and resonance-enhanced multiphoton ionization (REMPI) techniques: the TPD-REMPI method. The timing chart for TPD-REMPI experiments is shown in Figure 1. The temperature of the substrate was measured with a silicon diode and controlled with a fluctuation of less than 0.5 K. Prior to each measurement, the substrate was warmed to 55 K to remove O$_2$ molecules from the surface, since O$_2$ molecules are known to enhance the ortho-to-para conversion.

Figure 1. Schematic of the TPD-REMPI experiment. (a) Timing chart of the TPD-REMPI experiment. A series of molecular beam pulses of normal H$_2$ are first deposited on an Mg$_2$SiO$_4$ sample maintained at 10–18 K. After a certain waiting time ($t_{w,t} = 10–810$ s), the temperature of the substrate is raised to a 20 K minute$^{-1}$ ramping rate; this process is the so-called TPD process. The laser for REMPI is always operating during each run with a 10 Hz repetition rate and a pulse energy of 200 μJ. The H$_2$ molecules desorbed during a TPD run, i.e., at $t = t_{w,t} + t_{TD}$, are rotational-state selectively ionized to H$_2^+$ by the REMPI laser and detected with a linear time-of-flight spectrometer. (b) Schematic for the H$_2$ deposition (top) and TPD-REMPI (bottom) processes.

### 3. Results and Discussion

#### 3.1. Determination of NSC Time Constants

The experimental results obtained at 10 K are presented in Figure 2. Figure 2(a) shows a series of TPD-REMPI data measured for $t_{w,t} = 10$, 410, and 810 s. The growth of the $J = 0$ signal and decay of the $J = 1$ signal with increasing $t_{w,t}$ are readily recognized. The time variation of integrated TPD-REMPI signals is plotted in Figure 2(b). The sum of the $J = 0$ and $J = 1$ signals is constant within the experimental error, ensuring that accumulation of background H$_2$ during the waiting time and desorption upon NSC are negligible. Consequently, the decay of the $J = 1$ signal is attributed to the ortho-to-para conversion.

When the temperature of the substrate is sufficiently low such that thermal desorption can be ignored, the number density of o-H$_2$ ($J = 1$) decreases with time due to ortho-to-para conversion, while that of p-H$_2$ ($J = 0$) increases. This situation is applicable to temperatures of 10, 12, and 14 K in the present experiments. Thus, if one monitors the number density, $[o$-H$_2]$$_p$, it shows a single exponential decay,

$$[o$-H$_2]$$_p = [o$-H$_2]_0 \exp(-k_{op}t),$$

where $k_{op}$ is the ortho-to-para conversion rate constant and $[o$-H$_2]$$_p + [p$-H$_2]_p = [o$-H$_2]_0 + [p$-H$_2]_0 = \text{const.}$ Fitting of the decay of the $J = 1$ TPD-REMPI signal by a single exponential function gives a decay time constant $(1/k_{op}) = 980 \pm 90$ s at 10 K. The OPR, $\sim 1.8$, for $t_{w,t} = 10$ s is already smaller than the statistical value of 3 because NSC proceeds even during the TPD run. As detailed in Appendix A.2, this enhancement has little effect on the obtained time constants.
The time variation of TPD-REMPI signals for temperatures of 12, 14, 16, and 18 K are presented in Figure 3. As shown in Figures 3(a) and (b), the sum of the \( J = 0 \) and \( J = 1 \) TPD-REMPI signals is constant at 12 and 14 K, similar to the case at 10 K. Thus, the decay of the \( J = 1 \) TPD-REMPI signal can be fitted by Equation (1) to obtain decay time constants of 560 ± 60 and 360 ± 20 s for 12 and 14 K, respectively.

At 16 and 18 K (Figures 3(c) and (d)), decay of the sum as a function of \( t_{\text{wa}} \) is observed. This decay is presumably due to thermal desorption during the waiting time. In this case, differential rate equations for the surface number densities of \( o-H_2 \) and \( p-H_2 \) are written as follows:

\[
\frac{d[o-H_2]}{dt} = -k_{\text{sub}}[o-H_2] - k_{\text{OP}}[o-H_2],
\]

\[
\frac{d[p-H_2]}{dt} = -k_{\text{sub}}[p-H_2] + k_{\text{OP}}[o-H_2],
\]

where \( k_{\text{sub}} \) is the rate constant for unimolecular sublimation, which is assumed to be the same for \( o-H_2 \) and \( p-H_2 \); in reality, \( k_{\text{sub}} \) for \( o-H_2 \) might be smaller because of a slightly large binding energy, as deduced from the TPD spectra. Equation (2) is readily integrated to become

\[
[o \cdot H_2] = [o \cdot H_2]_0 e^{-(k_{\text{sub}} + k_{\text{OP}})t}.
\]

An integration of the sum of Equations (2) and (3) gives the following equation for the total \( H_2 \) on the surface:

\[
[H_2] = [o-H_2]_0 + [p-H_2]_0 = [H_2]_0 e^{-k_{\text{sub}}t}.
\]

Therefore, the sublimation rate constant \( k_{\text{sub}} \) is obtained from single exponential fitting of the decay of \([H_2]_0\) (i.e., the sum of \([o-H_2]_0\) and \([p-H_2]_0\)) and \( k_{\text{sub}} + k_{\text{OP}} \) is obtained from fitting of the decay of \([o-H_2]_0\). Consequently, the ortho-to-para conversion time constant, \( 1/k_{\text{OP}} \), is determined. Accordingly, the time constant for NSC was extracted from the fitting of \( J = 1 \) and the sum to be 290 ± 20 and 260 ± 70 s for 16 and 18 K, respectively, whereas the time constants for sublimation \((1/k_{\text{sub}})\) were 3300 ± 200 and 400 ± 80 s.

3.2. Comparison of NSC Time Constants

The NSC time constants determined in this work for an amorphous Mg_2SiO_4 surface are plotted as a function of substrate temperature in Figure 4, together with those reported for an amorphous solid water (ASW) (Ueta et al. 2016). These time constants are listed in Table 1. The time constants for the Mg_2SiO_4 surface are smaller than those for the ASW surface by a factor of 2–3. In the case of ASW, the time constant significantly decreases in the 9.2–12 K region and remains constant above 12 K. In the case of Mg_2SiO_4, we observe a gradual decrease in time constant as a function of temperature in the investigated temperature range (10–18 K). Because of fast unimolecular sublimation, we were unable to determine the time constant above 18 K. However, an analysis described in Appendix A.2 indicates that the time constant would not be smaller than 200 s even at the sublimation temperature (20–26 K) in the TPD runs. For comparison, we measured the NSC of D_2 at 18 K (Appendix A.3). The time constant is much larger than that of H_2 at 18 K, consistent with previous experiments on ASW (Sugimoto & Fukutani 2011; Ueta et al. 2016).

3.3. Temperature Dependence of NSC Rate

The ortho-to-para conversion of H_2 on a surface involves the NSC and subsequent energy dissipation processes. The presence of a magnetic field is known to enhance the NSC process (Fukutani & Sugimoto 2013). Because an Mg_2SiO_4 film does not have a magnetic moment and an adsorption of paramagnetic O_2 molecules is avoided, such an enhancement would be negligible in the present experiment. However, we cannot exclude magnetic moments induced by defects near the sample surface. To discuss the effect of such magnetic moments, an extensive surface characterization is required. The mechanisms of NSC on nonmagnetic surfaces have been theoretically discussed in recent years, but they are not yet conclusive (Sugimoto & Fukutani 2011; Ilisca & Ghiglieri 2014; Ilisca 2018). Clarifying it is outside the scope of this paper. Here we focus our discussion on the mechanism of the energy dissipation process required for the NSC. The energy gap between the \( J = 1 \) and \( J = 0 \) states is 14.7 meV (≈170 K) for the isolated H_2 but may become smaller due to the suppression of rotational motion for H_2 adsorbates. Therefore, the corresponding energy should be released into the solid. The presence of temperature dependence (Figure 4) indicates that phonons play a role in the energy dissipation process.
Spin-lattice relaxation will occur through one- or two-phonon processes. In the one-phonon process, the excess energy associated with the NSC process is transferred to the surroundings (i.e., phonon excitation in the thermal bath). Depending on the energy matching condition between the excess energy and phonon modes of the surroundings, the one-phonon process shows two distinct temperature dependences (Scott & Jeffries 1962). When there is a satisfactory match between them, the one-phonon process is known to show a temperature dependence of NSC rate as $k_{np}(T) = A \times T \coth \left( \frac{\Delta}{T} \right)$, where $T$ is the solid temperature and $\delta$ is the energy gap between these two spin states. On the other hand, when there is a mismatch between them, the process becomes a slower phonon-limited “bottleneck” process. This process shows a distinct temperature dependence, $k_{op}(T) = A \times T^n (n \sim 2)$.

The two-phonon process proceeds via the simultaneous absorption (from the initial state ($J = 1$) to the intermediate state) and emission (from the intermediate state to the final state ($J = 0$)) of phonons. Based on whether the intermediate state is real (i.e., $J = 2$ state) or virtual, the process is classified into the Orbach or Raman process, respectively. The NSC rate of the Orbach process follows $k_{op}(T) = A \times \exp \left( -\frac{\Delta}{T} \right)$, where $\Delta$ corresponds to the energy gap between the initial and intermediate states (Scott & Jeffries 1962). On the other hand, the Raman process shows a power-law dependence, $k_{op}(T) = A \times T^n (n = 7 \text{ or } 9)$. For example, Ueta et al. (2016) attributed the temperature dependence observed for H$_2$ NSC on ASW to this process (Figure 4).

Among the phonon processes described above, the one-phonon process expressed by $k_{np}(T) = A \times \coth \left( \frac{\Delta}{T} \right)$ can be excluded because it becomes almost temperature-independent in the present experimental condition, where $\delta = 170$ K and $10$ K $\leq T \leq 18$ K. The Orbach process ($k_{op}(T) = A \times \exp \left( -\frac{\Delta}{T} \right)$) with $\Delta = 339$ K

![Figure 3](image-url)
Then, we dissipated into the Mg$_2$SiO$_4$ bath. We note that this will not be the condition because the exact energy gap for H$_2$ on a Mg$_2$SiO$_4$ surface, since the NSC of molecules on the surface is complicated; e.g., several mechanisms have been suggested to explain the observed H$_2$ NSC rates on ASW (Sugimoto & Fukutani 2011; Ueta et al. 2016; Ilisca 2018).

3.4. Efficiency of Ortho-to-para Conversion under Astrophysical Environments

In star-forming regions, almost all hydrogen is present as H$_2$ in the gas phase rather than on grain surfaces because of the very low H$_2$--H$_2$ surface binding energy ($\sim$100 K; Lee et al. 1971) and the limited number of binding sites per H$_2$ molecule ($\sim$10$^{-4}$ sites per H$_2$). Here we derive the rate (cm$^{-3}$ s$^{-1}$) at which NSC on grain surfaces affects the gas-phase H$_2$ OP by under astrophysical environments using the experimentally derived $k_{\text{OP}}$. We denote the rate as $R_{\text{OP}}$, where $\alpha$ and $\beta$ indicate either ortho or para. Here $R_{\text{OP}}$ depends on the (i) collision rate of gaseous H$_2$ with grain surfaces ($R_{\text{coll}}$), (ii) sticking probability ($S$), (iii) ortho-to-para conversion time constant, and (iv) sublimation timescale of adsorbed H$_2$ and can be described as (Fukutani & Sugimoto 2013; Bovino et al. 2017; Furuya et al. 2019),

$$R_{\text{OP}} = \eta_{\alpha \rightarrow \beta} (1 - \Theta) S R_{\text{coll}} (\alpha \rightarrow H_2),$$

where $\Theta$ is the fraction of adsorption sites occupied by H$_2$. We consider the factor ($1 - \Theta$) in Equation (6), assuming that only one H$_2$ molecule is allowed to be adsorbed per adsorption site. Then, the product $(1 - \Theta) S R_{\text{coll}} (\alpha \rightarrow H_2)$ expresses the adsorption rate of H$_2$. The term $\eta_{\alpha \rightarrow \beta}$ represents the yield of gaseous $\alpha$-H$_2$ ($p$-H$_2$) per $p$-H$_2$ ($\alpha$-H$_2$) adsorption, which depends on the competition between NSC and sublimation of adsorbed H$_2$. To determine $\eta_{\alpha \rightarrow \beta}$ under astrophysical environments, we basically follow the procedure developed in our previous work, in which the NSC of H$_2$ on an ASW surface was studied (Furuya et al. 2019).

The surface coverage of H$_2$ is expected to be in adsorption--desorption equilibrium, since the surface adsorption site density is $\sim$10$^{10}$ sites cm$^{-2}$ and the H$_2$ flux (the time integral of the H$_2$ flux) on grain surfaces reaches this value in a very short timescale ($\sim$10 (10$^3$ cm$^{-3}$/n(H$_2$)) yr) compared to the dynamical timescale (i.e., the lifetime of MCs). Under adsorption--desorption equilibrium, the H$_2$ OP of the gas desorbing from the surface can be expressed as

$$R_{\text{sub}} (\alpha \rightarrow H_2)/R_{\text{sub}} (p \rightarrow H_2) = [(1 - \eta_{\alpha \rightarrow p}) f_\alpha + \eta_{\alpha \rightarrow p} f_p ]/[1 - \eta_{\alpha \rightarrow p} + (1 - \eta_{\alpha \rightarrow p}) f_p],$$

where $R_{\text{sub}}$ is the sublimation rate of H$_2$, and $f_\alpha$ and $f_p$ are the fractions of $\alpha$-H$_2$ and $p$-H$_2$, respectively, in adsorbing H$_2$ (or, equivalently, H$_2$ in the gas phase). With the relation $\eta_{\alpha \rightarrow p} = \eta_{\alpha \rightarrow p} \gamma$, where $\gamma$ is the thermalized value of the H$_2$ OP, one can obtain

$$\eta_{\alpha \rightarrow p} = [f_\alpha - f_p R_{\text{sub}} (\alpha \rightarrow H_2)/R_{\text{sub}} (p \rightarrow H_2)] / (1 + R_{\text{sub}} (\alpha \rightarrow H_2)/R_{\text{sub}} (p \rightarrow H_2)).$$

We quantify $R_{\text{sub}} (\alpha \rightarrow H_2)$ and $R_{\text{sub}} (p \rightarrow H_2)$ using the numerical simulations described below, followed by evaluation of $\eta_{\alpha \rightarrow p}$ and $\eta_{\alpha \rightarrow p}$, from Equation (8).

We numerically solve a set of rate equations for $\alpha$-H$_2$ and $p$-H$_2$ that describe the adsorption of gaseous H$_2$, thermal
desorption, thermal hopping, and NSC of adsorbed H$_2$, considering various adsorption sites with different potential energy depths on surfaces (see Equations (6) and (7) in Furuya et al. 2019). Regarding chemical species, only o-H$_2$ and p-H$_2$ in the gas phase and on grain surfaces are considered in this model. Initially, all H$_2$ is assumed to be in the gas phase with an OPR of 3; i.e., $f_o$ and $f_p$ are 0.75 and 0.25, respectively. For the binding energy distribution of H$_2$, we use the experimentally determined binding energy distribution of HD on amorphous MgFeSiO$_4$ in the literature (Figure 5; He & Vidali 2014). The hopping-to-binding energy ratio ($\chi$) is poorly constrained, and here we assume a conservative value of 0.8. The choice of the exact value of $\chi$ does not significantly affect our simulation results because $\eta_{o\rightarrow p}$ is close to unity even for $\chi = 0.8$ (see below) and a lower $\chi$ tends to lead to a higher $\eta_{o\rightarrow p}$ (Furuya et al. 2019). The sticking probabilities of H$_2$ to silicate and ASW are taken from Chaabouni et al. (2012) and He et al. (2016), respectively.

We run a small grid of pseudo-time-dependent simulations (i.e., the gas density and temperature are fixed with time in each simulation), varying the temperature from 10 to 20 K, and evaluate $\eta_{o\rightarrow p}$ using Equation (8). For temperatures from 10 to 18 K, we adopt the measured NSC time constant or the linearly interpolated value. Above 18 K, we assume that the time constant is the same as that at 18 K. As shown in Figure 6(a), $\eta_{o\rightarrow p}$ is close to unity; i.e., every o-H$_2$ collision leads to NSC, up to 18 K. The $\eta_{o\rightarrow p}$ decreases at higher temperatures and is $\sim$0.25 at 20 K. For the evaluation of $\eta_{o\rightarrow p}$, we chose the time at which the total H$_2$ flux reaches $10^7$ cm$^{-2}$, corresponding to the duration time of $\sim$100 (10$^3$ cm$^{-3}$/n(H$_2$)) yr. By this time, the H$_2$ coverage on the surface reaches adsorption–desorption equilibrium under all physical conditions explored here. We confirmed that $\eta_{o\rightarrow p}$ does not change with time once the system reaches adsorption–desorption equilibrium. For an ASW surface, $\eta_{o\rightarrow p}$ is close to unity only at surface temperatures lower than 13 K. The higher $\eta_{o\rightarrow p}$ for silicate than for ASW at a given temperature is due to (i) the smaller ortho-para conversion time constant, as found in this work (Figure 4), and (ii) the higher binding energy (Figure 5).

The yield of p-H$_2$ per o-H$_2$ collision with silicate (i.e., $\eta_{o\rightarrow p}(1 - \Theta)S$) is shown in Figure 6(b). The yield for silicate takes the maximum value of $\sim$0.8 at $\sim$14–18 K. In other words, every o-H$_2$ collision with silicate surfaces produces approximately one p-H$_2$ in the temperature range between 14 and 18 K; i.e., the timescale in which NSC on grain surfaces affects the gas-phase H$_2$ OPR ($\tau_{op} = n(o-H_2)/R_{surf}$) is comparable to the collisional timescale of o-H$_2$ with grain surfaces ($\sim$3 (10$^3$ cm$^{-3}$/n$_H$) Myr, where n$_H$ is the number density of hydrogen nuclei). At warmer temperatures, the residence time of H$_2$ on surfaces is too short for NSC. At lower temperatures, the exchange of gaseous and icy H$_2$ is inefficient (i.e., $\Theta$ is high; adsorbed H$_2$ does not desorb and hinders other gaseous H$_2$ from being adsorbed). At a given temperature, $\Theta$ increases with increasing H$_2$ gas density. This is the reason why the yield is slightly lower at the H$_2$ gas density of 10$^3$ cm$^{-3}$ compared to that at 10$^3$ cm$^{-3}$.

### 3.5. Astrophysical Implication

In the interstellar medium (ISM), H$_2$ predominantly forms via recombination of two H atoms on grain surfaces and desorbs into the gas phase. The conversion of H atoms into H$_2$ molecules finishes before the dust grains are coated by ice mantles (e.g., Furuya et al. 2015; Hocuk & Cazaux 2015). The OPR of H$_2$ upon formation on the surfaces is 3 (Watanabe et al. 2010). The dust temperature observed in the diffuse ISM is $\sim$20 K, and it is lower in MCs (15–17 K; Planck Collaboration et al. 2014). We expect that the NSC of H$_2$ on bare grain surfaces affects the H$_2$ OPR from the formation stage of H$_2$ (i.e., in MCs); the NSC rate ($\tau_{op}$n(o-H$_2$)) should be comparable to or greater than the H$_2$ formation rate on grains ($R_{form}(H_2)$) when n(o-H$_2$) $>$ n (atomic H) because the H$_2$ formation rate is given by half the adsorption rate of atomic H on grain surfaces, while the NSC rate is very close to the collisional rate of o-H$_2$ to the grain surfaces.

To confirm this, we consider a simple model of the evolution of o-H$_2$ and p-H$_2$ in the gas phase, where only the H$_2$ formation on grain surfaces and NSC of H$_2$ on grain surfaces are taken into account:

$$\frac{dn(o-H_2)}{dt} = b_o R_{form}(H_2) - R_{surf} + R_{surf} - R_{surf}$$

$$\frac{dn(p-H_2)}{dt} = b_p R_{form}(H_2) + R_{surf} - R_{surf}$$

$$\frac{dn(atomic H)}{dt} = -2R_{form}(H_2),$$

where $b_o$ and $b_p$ are the branching ratios to form o-H$_2$ and p-H$_2$, respectively, for H$_2$ formation on grain surfaces. We solve the above ordinary differential equations under the physical conditions appropriate for MCs, n$_H = 10^3$ cm$^{-3}$, and gas and dust temperatures of 15 K. It should be noted that our model does not consider the formation of ice layers, and we assume that dust grains are always bare. In reality, dust grains are covered by ice at some point, and after that, the NSC on bare grains is no more relevant. In the ISM, two types of dust grains exist: silicate and carbonaceous materials. We treat all bare grains as silicate in this model, and the total cross section per H nuclei is set to 1 x 10$^{-22}$ cm$^{-2}$. The NSC on amorphous diamond-like carbon surfaces was observed in our previous experiments (Tsuge et al. 2019), but the time constant was not derived. The time evolution of the atomic H and H$_2$ abundances and the H$_2$ OPR are shown in Figure 7. As expected, when n(H$_2$) $\sim$ n(atomic H), the H$_2$ OPR is already lower than 3.

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**Figure 5.** Binding energy distribution of H$_2$ on surfaces. The binding energy distribution of H$_2$ on silicate (red line) adopted in our numerical simulations is shown along with that on ASW (black line) for comparison. The data were taken from He & Vidali (2014).

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**Figure 6.** Relative weight of H$_2$ on grain surfaces. The relative weight of H$_2$ on silicate (red line) and ASW (black line) is shown as a function of binding energy. The binding energy distribution of H$_2$ on silicate is shown as a red line, and the binding energy distribution of H$_2$ on ASW is shown as a black line. The data were taken from He & Vidali (2014).
Since the density dependence of $R_{\text{surf}}$ and $R_{\text{dissolv}}(\text{H}_2)$ is the same, this result does not depend on the chosen density. The results indicate that the NSC of H$_2$ on silicate surfaces is rapid enough to reduce the H$_2$ OPR to lower than 3 when the conversion of H atoms into H$_2$ occurs in the ISM.

The NSC of H$_2$ also occurs in the gas phase via proton exchange reactions with H$^+$ and H$_3^+$ (Hugo et al. 2009; Honvault et al. 2011). After the dust grains are covered by ice, the NSC of H$_2$ occurs at least on ASW (Watanabe et al. 2010). In order to reveal the contribution of each process to the evolution of the H$_2$ OPR, astrochemical simulations of the MC formation with the NSC processes of H$_2$ both on grain surfaces and in the gas phase are demanded. Such studies are postponed for future work.

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**Figure 6.** (a) Yields of $p$-H$_2$ per o-H$_2$ adsorption ($y_{p-o}$) as functions of temperature. The red line shows the yield for silicate (this work), while the black line shows that for ASW (Furuya et al. 2019) for comparison. The H$_2$ gas density is assumed to be 10$^3$ cm$^{-3}$, but the density dependence is very weak; the yields at 10$^3$ cm$^{-3}$ are almost identical to those at 10$^3$ cm$^{-3}$. (b) Production yields of $p$-H$_2$ per o-H$_2$ collision as functions of temperature. The solid lines represent the values at the H$_2$ gas density of 10$^3$ cm$^{-3}$, while the dashed lines represent the values at 10$^4$ cm$^{-3}$.

**Figure 7.** Time evolution of the atomic H (dashed black line) and H$_2$ (solid black line) abundances and the H$_2$ OPR (red line) predicted by our simple model (see the main text). The density of hydrogen nuclei ($n_H$) is set to 10$^3$ cm$^{-3}$, and the gas and dust temperatures are set to 15 K.

**Appendix**

A.1. Preparation and Characterization of the Amorphous Mg$_2$SiO$_4$ Film

The amorphous Mg$_2$SiO$_4$ film was prepared on an aluminum substrate by pulsed laser ablation in the main chamber. During sample preparation, an Mg$_2$SiO$_4$ target was placed near the aluminum substrate at an approximately 40 mm distance and a 45° angle. The rotating target was irradiated with a pulsed laser beam (532 nm wavelength, 8 ns pulse width, 10 Hz repetition rate, and 20 mJ pulse energy) focused with an $f$ = 300 mm lens. Typically, laser ablation was performed for 12,000 pulses, resulting in a film with a few tens of nanometers thick on the aluminum substrate.

To characterize the samples by transmission electron microscopy (TEM), a thin film of Mg$_2$SiO$_4$ was prepared on a thin carbon film with a thickness of less than 6 nm on a copper mesh grid for TEM observation. A TEM apparatus (JEOL, JEM-2100F) was used with a field emission gun at an acceleration voltage of 200 kV, which was equipped with energy dispersive X-ray spectroscopy (EDS) for chemical composition analysis (JEOL, JED2300T). The TEM analysis results are summarized in Figure A1. The bright-field image (Figure A1(a)) shows that the sample was composed of ∼99.7% homogeneous regions and ∼0.3% high-contrast particles by area ratio. The Mg/Si ratio of the homogeneous regions was analyzed by EDS and found to be 1.86. We obtained the electron diffraction patterns of a homogeneous region using a thicker sample fabricated by the same method (Figure A1(b)). The electron diffraction pattern shows a halo pattern that represents an amorphous structure. The intensity line profile of the electron diffraction pattern (Figure A1(b), inset) shows a hump, which probably originates from a peak (2.88 Å) due to amorphous Mg$_2$SiO$_4$ (Igami et al. 2020).

The surface adsorption site density of the amorphous Mg$_2$SiO$_4$ film was estimated to be ∼10$^{16}$ sites cm$^{-2}$ according to the method described elsewhere (Hama et al. 2012; Tsuge et al. 2019), in which the known site density of an Al surface (1.2 × 10$^{15}$ sites cm$^{-2}$; Wyckoff 1931) was used as a reference. This value is similar to that of the porous ASW surface, indicating the roughness of the film.
Figure A1. A TEM analysis of the amorphous Mg$_2$SiO$_4$ film. (a) Bright-field TEM image of the amorphous Mg$_2$SiO$_4$ film. The region enclosed by the black dashed line and the particle indicated by white arrowhead were analyzed by EDS, and the Mg/Si ratios are 1.86 and 1.74, respectively. The scale bar is 2 μm. (b) Electron diffraction pattern of a homogeneous region in the amorphous Mg$_2$SiO$_4$ film. The white dashed line corresponds to a d-spacing of 2.88 Å. The inset shows the normalized intensity line profile between the center of the diffraction pattern and the edge in the horizontal direction. The horizontal axis of the inset corresponds to the scale of the diffraction pattern along the horizontal direction.

A.2. The Effect of NSC during TPD Process

Because in the TPD-REMPI measurements, we monitor the number density of o-H$_2$ upon sublimation, i.e., at $t = t_{w.t.} + t_{TPD}$ defined in Figure 1, the measured number density of o-H$_2$ is different from that at $t = t_{w.t.}$. From Equation (1), the number density of o-H$_2$ after a certain waiting time ($t = t_{w.t.}$) is derived as $[o-H_2]_{t=t_{w.t.}} = [o-H_2]_0 e^{-k_{OP} t_{w.t.}}$. During a TPD run, ortho-to-para conversion is accelerated. When we ignore the temperature (time) dependence of the conversion rate during TPD, the time evolution of $[o-H_2]$ is described as

$$[o-H_2]_{t=t_{w.t.}+t_{TPD}} = [o-H_2]_0 e^{-k_{OP} t_{w.t.}} e^{-k' t_{TPD}}, \quad \text{(A1)}$$

where $k'$ is the ortho-to-para conversion rate constant during TPD. By taking the logarithm of Equation (A1), we obtain

$$\ln([o-H_2]_{t=t_{w.t.}+t_{TPD}}/[o-H_2]_0) = -k_{OP} t_{w.t.} - k' t_{TPD}. \quad \text{(A2)}$$

This relation suggests that a plot of $\ln([o-H_2]_{t=t_{w.t.}+t_{TPD}}/[o-H_2]_0)$ versus $t_{w.t.}$ gives a linear relation, and the rate constants $k_{OP}$ and $k'$ can be determined from the slope and intercept, respectively.

The experimental data obtained at 10 K (those shown in Figure 2(b)) are plotted in Figure A2. As expected, a plot of $\ln([o-H_2]_{t=t_{w.t.}+t_{TPD}}/[o-H_2]_0)$ versus $t_{w.t.}$ shows a linear relation, and from the slope and intercept, we obtain $1/k_{OP} = 1050 \pm 90$ s and $1/k' = 220 \pm 50$ s. The $1/k_{OP}$ value (1050 ± 90 s) agrees well with the time constant (980 ± 90 s) determined from a single exponential fitting to $[o-H_2]_{t=t_{w.t.}+t_{TPD}}$, indicating that the latter value can be regarded as the time constant for ortho-to-para conversion during the waiting time. In addition, the ortho-to-para conversion time constant during the TPD run, $1/k' = 220 \pm 50$ s, which is slightly smaller than or equivalent to the constant determined for 18 K (260 ± 70 s), guarantees the validity of our analyses.

A.3. Para-to-ortho Conversion of D$_2$ on a Silicate Surface

Because D$_2$ is a boson due to two deuterons with nuclear spin 1, the nuclear spin state of 2 and 0 (ortho) and 1 (para) are only coupled with the rotational states of even and odd quantum numbers, respectively. Thus, at low temperatures, ortho- and para-D$_2$ are in the $J = 0$ and 1 states, respectively.

The para-to-ortho conversion of D$_2$ molecules on a silicate surface was investigated at 18 K. The time variation of the integrated TPD-REMPI signals is plotted in Figure A3. The sum of the $J = 0$ and $J = 1$ signals was constant within experimental error, ensuring that desorption of D$_2$ by thermal and upon NSC was negligible. Fitting of the $J = 1$ signal by a single exponential

Figure A2. Additional analysis of the $J = 1$ TPD-REMPI signal decay at 10 K. The values $\ln([o-H_2]_{t=t_{w.t.}+t_{TPD}}/[o-H_2]_0)$ are plotted vs. $t_{w.t.}$ according to Equation (A2). The linear regression analysis result is shown by the solid line.
A decay time constant of \(2200 \pm 300\) s. The NSC of D\(_2\) is much slower than H\(_2\), similar to that on the ASW surface, as previously reported (Sugimoto & Fukutani 2011; Ueta et al. 2016).

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