Hyperfine excitation of linear molecules by para- and ortho-H\(_2\): Application to the HCl–H\(_2\) system

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The determination of hyperfine structure resolved excitation cross sections and rate coefficients due to H\(_2\) collisions is required to interpret astronomical spectra. In this paper, we present several theoretical approaches to compute these data. An almost exact recoupling approach and approximate sudden methods are presented. We apply these different approaches to the HCl–H\(_2\) collisional system in order to evaluate their respective accuracy. HCl–H\(_2\) hyperfine structure resolved cross sections and rate coefficients are then computed using recoupling and approximate sudden methods. As expected, the approximate sudden approaches are more accurate when the collision energy increases and the results suggest that these approaches work better for para-H\(_2\) than for ortho-H\(_2\) colliding partner. For the first time, we present HCl–H\(_2\) hyperfine structure resolved rate coefficients, computed here for temperatures ranging from 5 to 300 K. The usual \(\Delta j_1 = \Delta F_1\) propensity rules are observed for the hyperfine transitions. The new rate coefficients will significantly help the interpretation of interstellar HCl emission lines observed with current and future telescopes. We expect that these new data will allow a better determination of the HCl abundance in the interstellar medium, that is crucial to understand the interstellar chlorine chemistry. © 2014 AIP Publishing LLC [http://dx.doi.org/10.1063/1.4898855]

I. INTRODUCTION

The determination of hyperfine structure resolved cross sections and rate coefficients for the collisions of two diatomic molecules is a very challenging task from both the theoretical and experimental points of view. Indeed, from the theoretical side, the number of coupled channels that need to be considered in the scattering calculations is usually extremely large so that exact calculations are very central processing unit (CPU) and memory demanding. From the experimental side, the very weak splitting between the hyperfine levels is usually very difficult to resolve using the current experimental tools. As a result, the hyperfine structure is neglected in most of the theoretical and experimental studies of scattering between two diatomic molecules.\(^1\)\(^-\)\(^4\)

In contrast, the hyperfine structure of the interstellar molecules is frequently resolved in the observational spectra thanks to the very high resolution of the present telescopes (see, e.g., CN,\(^5\) HCN/HNC,\(^6\)\(\_\)\(\_\)\(\_\)\(\_\)\(\_\)\(\_\)\(\_\)\(\_\)\(\_\)\(\_\)\(\_\)\(\_\)\(\_\)\(\_\) N\(_2\)H\(_+\),\(^7\)\(\_\)\(\_\)\(\_\)\(\_\)\(\_\)\(\_\) HCl\(^8\)). Such observations provide useful information for the astronomers on the physical and chemical conditions in the interstellar medium. In particular, determining the relative intensities of the hyperfine lines allows the determination of molecular abundance if local thermodynamical equilibrium, is fulfilled.\(^9\) However, the interpretation of the observed hyperfine spectrum requires most of the time detailed radiative transfer calculations, which cannot be performed without a knowledge of the hyperfine collisional rate coefficients, in addition to the hyperfine radiative rates. A comprehensive understanding of collisional effects is therefore crucial to interpret molecular hyperfine spectra (see the review of Roueff and Lique\(^11\)).

The main colliding partner in the interstellar medium is the H\(_2\) molecule. Computation of hyperfine structure resolved cross sections and rate coefficients due to collisional excitation by He [as a model for H\(_2\)] and para-H\(_2\)(\(j = 0\)) have been performed for a number of species: CN,\(^12\)\(^-\)\(^3\) HCN,\(^4\) HCl,\(^5\)\(\_\)\(\_\)\(\_\)\(\_\)\(\_\)\(\_\)\(\_\) NH,\(^14\) N\(_2\)O,\(^15\) N\(_2\)H\(_+\),\(^16\) C\(_2\)H\(_2\),\(^17\) or DCO\(^+\).\(^18\) It should be emphasized that, in all these calculations, the projectile was considered as a structureless species and did not imply any coupling of its angular momenta with the angular momentum of the target. A recent review on the different theoretical approaches to take into account the hyperfine structure in the case of collisions with a structureless projectile, was published recently by Faure and Lique.\(^22\)

However, in many cases, hyperfine structure resolved data are also needed for the H\(_2\) collisional partner in its excited rotational states. To the best of our knowledge, no hyperfine structure resolved cross sections and rate coefficients due to collisions with para-H\(_2\)(\(j > 0\)) or with ortho-H\(_2\) has been computed, except for the study of Offer et al.\(^23\) on the OH–H\(_2\) collisional system. The main aim of this paper is to review and compare different theoretical approaches to compute hyperfine collisional cross sections and rate coefficients. We intend to apply the theoretical approaches presented by Faure and Lique\(^22\) to the case of collisions between two diatomic molecules. In particular, these approaches allow the determination of hyperfine collisional data with the ortho-H\(_2\)(\(j = 1\)) collisional partner. These data are crucially needed for the interpretation of astronomical spectra. We then select the HCl–H\(_2\) collisional system as a benchmark for testing these methods. The choice of such system is particularly justified since approximate sudden methods (presented later in this paper) are not expected to work well for the HCl molecule, due to the large spacing between rotational/hyperfine levels. We

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could thus expect that the accuracy of the different theoretical approaches tested here are in their upper limit. As a consequence, it will really allow us to validate/invalidate the different theoretical approaches that could be used to deal with the hyperfine excitation of interstellar molecules by both para- and ortho-H₂.

In addition, the computation of collisional rate coefficients for the HCl molecule presented in this study has also some astrophysical motivations. HCl was first identified by Blake et al. in Orion Molecular Cloud 1 and the HCl lines can be used to trace very dense gas and protostellar shock regions. The precise estimation of the HCl abundance in molecular clouds is still an open question, but it will require accurate collisional rate coefficients to solve this problem. As HCl–H₂ rate coefficients strongly depends on the rotational states of H₂, it has been shown that the use of ortho-H₂ rate coefficients was crucially needed to accurately determine the HCl abundance in molecular clouds. Then, we expect that the present hyperfine data (the first with the H₂ collisional partner) will provide astronomers with new insights on the HCl abundance in the interstellar medium.

The paper is organized as follows: A description of the general methodology is presented in Sec. II. The comparison between the different methods is illustrated on the HCl–H₂ collisional system in Sec. III. Conclusions are drawn in Sec. IV.

II. METHODOLOGY

Exact quantum mechanical calculations of hyperfine structure resolved cross sections can be performed by introducing the hyperfine structure of the target in the Close Coupling (CC) scattering equations and then by solving them. However, as mentioned in the Introduction, such calculations are computationally intensive due to the very large number of channels that needs to be considered. In this paper, we focus on the computation of hyperfine structure resolved cross sections and rate coefficients from S-matrices, cross sections or rate coefficients obtained from nuclear spin-free calculations. Indeed, most of the scattering calculations between two diatomic molecules are performed by neglecting the nuclear spin of the target. Our goal is to show how hyperfine structure resolved collisional data can be obtained from these spin-free collisional data. In the remainder of this section, we present the different methods for this computation.

In this section, the subscript 1 refers to the first diatomic molecule (the target with non-zero nuclear spin) and the subscript 2 refers to the second diatomic molecule (the projectile). In this paper, the projectile will be the H₂ molecule but the formula can be used for any diatomic molecule.  and  refer to the initial and final rotational states of the target, respectively, while  and  refer to the initial and final rotational states of the projectile, respectively.

The hyperfine structure levels of the target are labeled with  and  where  is the total molecular angular momentum quantum number of the target, is defined as  and  the total hyperfine quantum number, respectively.

A. Recoupling approach

The hyperfine splitting of the rotational energy levels is usually very small. Hence, if the hyperfine levels can be assumed to be degenerate, the hyperfine scattering problem can be considerably simplified. Thus, the integral cross sections corresponding to transitions between hyperfine levels of the target can be obtained from nuclear spin free S-matrices using a recoupling method. The recoupling scheme of the angular momenta is then adopted to transform S-matrices to a new recoupled basis as described in Refs. 23 and 31.

We start by coupling the rotational angular momenta of the two diatomic molecules to form  and , which then couples with the relative angular momentum of these molecules,  to form the total angular momentum  (without nuclear spin of the target). The total angular momentum of a system including nuclear spin is, then, given by

\[ J_T = J + I_1. \] (1)

In the recoupling scheme, we introduce a new perturbing angular momentum  and recouple the angular momenta as follows:

\[ J_R = J_2 + I_1, \quad J_T = J_R + F_1. \] (2)

Transformation to the new basis leads to the recoupling of S-matrices obtained from nuclear spin free CC calculations, where

\[
S^{[J_1(J_2I)]}_T(J_R,J_T,F_1) = \sum_{J_1,J_2,J_R} \left( -1 \right)^{J_1+J_2+I_1+I_2} \times \left[ 2F_1 + 1 \right] \left[ 2J_2 + 1 \right] \times \left[ 2J_R + 1 \right] \delta_{J_1 J_R} \delta_{J_2 J_T} \delta_{F_1 F_2} \delta_{I_1 I_2} \delta_{J_1 J_2} \delta_{J_R J_T} \times \left\{ \begin{array}{c} J_1 \ J_2 \\ J_R \end{array} \right\} \times \left\{ \begin{array}{c} I_1 \ J_T \\ F_1 \end{array} \right\} \times \left\{ \begin{array}{c} J_1 \ J_2 \\ I_1 \ J_T \\ F_1 \end{array} \right\} \right] \] (3)

where \( \{ \ldots \} \) is a “6-j” symbol and where \( S^{[J_1(J_2I)]}_T(J_R,J_T,F_1) \) are the S-matrices obtained from nuclear spin-free calculations.

Thus, the hyperfine-structure resolved cross sections are then given by

\[
\sigma_{J_1,J_2}^{Rec} = \frac{\pi}{k^2_{J_1,J_2}(2F_1 + 1)(2J_2 + 1)} \sum_{J_T} \left[ 2J_T + 1 \right] \times \left\{ \begin{array}{c} J_1 \ J_2 \\ J_T \end{array} \right\} \times \left\{ \begin{array}{c} I_1 \ J_T \\ F_1 \end{array} \right\} - S^{[J_1(J_2I)]}_T(J_R,J_T,F_1) \right|_{J_1=J_2,I_1=I_2}^2, \] (4)

where \( k^2_{J_1,J_2} = 2\mu(E - E_{J_1,J_2}) \). \( \mu \) is the reduced mass of the system, \( E \) is the total energy of the system, and \( E_{J_1,J_2} \) is the internal energy of the colliding system.
The summation extends over all values of the total angular momentum $J$, which contribute to the inelastic collisions. This approximate, but almost exact recoupling approach will be considered as our reference approach in the following. Indeed, it has been shown recently in the case of CN–H$_2$ collisions$^3$ that fine-structure resolved exact and recoupling cross sections are almost equal when energy levels splitting is very small ($\approx 10^{-2}$ cm$^{-1}$). Hyperfine splitting is usually even smaller ($\lesssim 10^{-4}$ cm$^{-1}$) so that we can be confident in the accuracy of this recoupling approach. However, it should be noted that the recoupling technique requires to store the S-matrices that can become prohibitively large for calculations at moderate and high temperatures, especially if the rotational constant of the molecule is small.

B. Infinite order sudden limit (IOS)

Hyperfine cross sections computed within the IOS approximation in which the rotational energy spacings are simply ignored can be directly deduced from the knowledge of the CC cross sections between rotational levels ($\sigma_{J_i,J_f}^{CC}$). Indeed, we can take advantage of the property of the IOS approximation that can provide all the transitions (rotational and hyperfine) from only the so-called “fundamental” cross sections,$^{32,33}$ which are the transitions out the lowest channel ($J_i = 0$ and $J_f = 0$). Such approximation is very popular since it allows to easily deal with any complex fine/hyperfine structures of molecules.

In practice, we can use the CC nuclear spin free cross sections $\sigma_{J_i,J_f}^{CC}$ to evaluate the “fundamental” cross sections. Excitation fundamental cross sections are also usually replaced by the de-excitation fundamental cross sections as follows:

$$\sigma_{0,0\rightarrow L_1,L_2}^{CC} = (2L_1 + 1)(2L_2 + 1)\sigma_{L_1,L_2\rightarrow 0,0}^{CC},$$

where $L_1$ and $L_2$ are the rotational state of the target and projectile, respectively.

Such procedure has been shown to improve the accuracy of the results at low collisional energies.$^{22}$

Using the IOS approximation, rotationally nuclear spin free inelastic cross sections are given by$^{33}$

$$\sigma_{J_i,J_f}^{IOS} = \sum_{L_1,L_2} (2J_1 + 1)(2J_2 + 1) \left( \sum_{J_1,J_2} \frac{(2J_1 + 1)(2J_2 + 1)}{2} \left( J_1 L_1 J_2^2 \right) \left( J_2 L_2 J_1^2 \right)^2 \text{det} \left( \begin{array}{ccc} 0 & 0 & 0 \\ 1 & 1 & 1 \\ 0 & 0 & 0 \end{array} \right) \right) \times (2L_1 + 1)(2L_2 + 1)\sigma_{L_1,L_2\rightarrow 0,0}^{CC},$$

where ( ) is a “3-j” symbol.

Hyperfine cross sections can then be obtained as follows:

$$\sigma_{J_i,F_i,J_f,F_f}^{IOS} = \sum_{L_1,L_2} \frac{(2J_1 + 1)(2J_2 + 1)}{2} (2L_i + 1) \left( J_2 L_2 J_1^2 \right)^2 \left( J_1 L_1 J_2^2 \right) \times (2F_i + 1) \left( J_2 L_2 J_1^2 \right)^2 \text{det} \left( \begin{array}{ccc} 0 & 0 & 0 \\ 1 & 1 & 1 \\ 0 & 0 & 0 \end{array} \right) \times (2L_1 + 1)(2L_2 + 1)\sigma_{L_1,L_2\rightarrow 0,0}^{CC}.$$  

Note that in Eqs. (6) and (7), $\sigma_{L_1,L_2\rightarrow 0,0}^{CC}$ can be replaced by nuclear spin free cross sections obtained from approximate coupled states calculations$^{34}$ or from any other theoretical methods used to determine state-to-state rotationally inelastic cross sections.

Note also that in Eqs. (6) and (7), it is possible to replace the cross sections $\sigma_{L_1,L_2\rightarrow 0,0}^{CC}$ by the corresponding thermal rate coefficients $k_{L_1,L_2\rightarrow 0,0}^{CC}(T)$ to obtain directly the hyperfine structure resolved rate coefficients. Rotational rate coefficients are usually tabulated in astrophysical databases$^{35,36}$ so that hyperfine rate coefficients may be easily obtained using the above procedure.

C. Scaled-infinite order sudden limit (S-IOS)

Generally, the rotational energy spacings in diatomic molecules (typically on the order of a few cm$^{-1}$) are not negligibly small. The IOS approximation is thus inaccurate at low energies, despite the use of CC cross sections instead of IOS fundamental cross sections. On the other hand, the hyperfine splittings are negligible compared to the collisional energies and the above IOS prescriptions are expected to correctly predict the relative cross sections among hyperfine levels within a rotational state.

Thus, the ratio between $\sigma_{J_i,F_i,J_f,F_f}^{IOS}$ and $\sigma_{J_i,F_i,J_f,F_f}^{IOS}$ could be assumed to be equal to the ratio between $\sigma_{L_1,L_2\rightarrow 0,0}^{CC}$ and $\sigma_{L_1,L_2\rightarrow 0,0}^{CC}$ for all the transitions. Then, one could scale the rotational CC cross sections with the ratio of hyperfine and rotational IOS cross sections in order to obtain a better estimate of the hyperfine cross sections

$$\sigma_{J_i,F_i,J_f,F_f}^{S-IOS} = \frac{\sigma_{J_i,F_i,J_f,F_f}^{S-IOS}}{\sigma_{L_1,L_2\rightarrow 0,0}^{CC}} \sigma_{L_1,L_2\rightarrow 0,0}^{CC}.$$  

Such procedure was first presented by Neufeld and Green$^{15}$ in the case of collisions with a structureless projectile. We refer to this method as S-IOS.

This scaling procedure ensures that the summed hyperfine rate coefficients are identical to the CC pure rotational rate coefficients, as in the case of the recoupling approach

$$\sum_{F_f} \sigma_{L_1,L_2\rightarrow 0,0}^{S-IOS} = \sigma_{L_1,L_2\rightarrow 0,0}^{CC}.$$  

D. $M_j$ randomizing limit

Finally, a very simple approach called the $M_j$ randomizing limit$^{30}$ has also been applied in the case of collisions with a structureless target. It consists in a statistical approach where the hyperfine cross sections do not depend on the initial hyperfine level. Using such approximation, the hyperfine cross sections are assumed to be proportional to the degeneracy of the final hyperfine level ($2F_f + 1$). In the case of collisions between two diatomic molecules, the hyperfine cross
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sections is then given by

$$
\sigma^{RAN}_{J_i,J_j \rightarrow \tilde{J}_i,J_j} = \frac{(2F_i'+1)}{(2J_i+1)(2J_j+1)} \sigma^{CC}_{J_i,J_j \rightarrow \tilde{J}_i,J_j}. \quad (10)
$$

However, it has been shown$^{22}$ that this statistical method leads to up to two orders of magnitude differences compared to a recoupling approach, principally due to the lack of respect of the propensity rules in favor of $\Delta J_1 = \Delta F_1$. Hence, it is not recommended to use this approximation and we do not discuss anymore the validity of this method in the following.

### III. APPLICATION TO THE HCl–H$_2$ COLLISIONAL SYSTEM

As a first application, we use the HCl–H$_2$ nuclear spin free S-matrices, cross sections, and rate coefficients recently computed by some of us$^{27,28}$ in order to compute hyperfine structure resolved HCl–H$_2$ collisional data. The different theoretical approaches presented above are applied and compared, to evaluate their accuracy.

The HCl–H$_2$ nuclear spin free scattering calculations were based on a potential energy surface$^{28}$ computed at the coupled cluster with single, double, and perturbative triple excitations [CCSD(T)]$^{37,38}$ level of theory using the rather large augmented correlation-consistent quadruple zeta (aug-cc-pVQZ) basis set$^{39}$ augmented with bond functions.$^{40}$ CC rotationally inelastic S-matrices and cross sections between the first 11 rotational levels of HCl were obtained for energies up to 3000 cm$^{-1}$. Corresponding rate coefficients were provided for temperatures up to 300 K.

In HCl, the coupling between the nuclear spin ($I_1 = 3/2$) of the chlorine atom and the molecular rotation results in a weak splitting of each rotational level $j_1$ into 4 hyperfine levels (except for the $j_1 = 0$ level which has only 1 hyperfine level and for the $j_1 = 1$ level which is split into only 3 levels). Each hyperfine level is designated by a quantum number $F_1$ ($F_1 = I_1 + j_1$) varying between $|I_1 - j_1|$ and $I_1 + j_1$. In the following, $j_2$ designates the rotational momentum of the H$_2$ molecule. Note that atomic hydrogen also possess a non-zero nuclear spin. However, the hyperfine splitting due to hydrogen nuclear spin is much smaller than the one due to chlorine nuclear spin and cannot be resolved by actual telescopes.

First, we compute hyperfine structure resolved cross sections using the recoupling approach. We use the S-matrices computed in Lanza et al.$^{28}$ to obtain the recoupling cross sections using Eqs. (3) and (4). The calculations are limited to rotational levels with $j_1, j'_1 \leq 5$. We only consider the transitions where $j_2$ remains constant, and equal to 0 (para-H$_2$) and 1 (ortho-H$_2$).

![Comparison between HCl–para-H$_2$](image1.png)

**FIG. 1.** Comparison between HCl–para-H$_2$ (j$_1$ = 0) recoupling and IOS hyperfine cross sections for all the de-excitation transitions up to $j_1 = 5$ at four different collisional energies. The vertical axis represents the hyperfine IOS cross sections and the horizontal axis represents the corresponding hyperfine recoupling cross sections. The two dashed lines in each panel delimit the region where the cross sections differ by less than a factor of 3.
From the latter cross sections, we obtain the corresponding thermal rate coefficients at temperature \(T\) by averaging over the collision energy \(E_c\)

\[
k^\text{Rec}_{F_1',F_2',J_1',J_2'}(T) = \left( \frac{8}{\pi \mu k_B T^3} \right)^{\frac{1}{2}} \times \int_0^\infty \sigma^\text{Rec}_{F_1',F_2',J_1',J_2'} E_c e^{\frac{E_c}{T}} dE_c,
\]

where \(\sigma^\text{Rec}_{F_1',F_2',J_1',J_2'}\) is the hyperfine structure resolved cross section, \(\mu\) is the reduced mass of the system, and \(k_B\) is the Boltzmann’s constant. Calculations up to 3000 cm\(^{-1}\) allow determining rate coefficients from 5 to 300 K.

In the following, we compare our IOS and S-IOS results to the results obtained from the recoupling approach (taken as our reference).

Second, we use the nuclear spin free CC cross sections and rate coefficients of Refs. 27 and 28 to compute pure IOS hyperfine cross sections \(\sigma^\text{IOS}_{F_1',F_2',J_1',J_2'}\) and rate coefficients \(k^\text{IOS}_{F_1',F_2',J_1',J_2'}\).

Figs. 1 and 2 show a comparison between hyperfine recoupling and hyperfine IOS cross sections for all the de-excitation transitions up to \(J_1 = 5\), including quasi-elastic transitions (those with \(J_1 = J_1\) and \(F_1 \neq F_1'\)). Fig. 1 presents the results for collisions with para-H\(_2\)(\(J_2 = 0\)) and Fig. 2 shows the results for collisions with ortho-H\(_2\)(\(J_2 = 1\)).

Significant differences exist between recoupling and IOS data for both para- and ortho-H\(_2\) colliders, the differences being more pronounced for ortho-H\(_2\) than for para-H\(_2\). For collisions with ortho-H\(_2\)(\(J_2 = 1\)), IOS approach fails to properly estimate the hyperfine cross sections for most of the transitions. The mismatch is larger than a factor of 10 for many transitions, despite a slight improvement with increasing energies. For collisions with para-H\(_2\)(\(J_2 = 0\)), the mean difference is smaller than for collisions with ortho-H\(_2\)(\(J_2 = 1\)). However, significant deviations from the recoupling results still exist at low energies. As expected, the agreement between the two sets of cross sections tends to improve with increasing energies. For kinetic energies larger than 200 cm\(^{-1}\), the differences are usually less than a factor of 2-3.

Such results are not surprising as we do not expect that the IOS approximation is accurate for light molecules like HCl with large energy spacing between energy levels as well as for low and moderate collisional energies. As a result, the IOS methodology does not provide an accurate description of the rotational and hyperfine cross sections. IOS approach may be more suited for heavier targets such as HCN, HNC, or N\(_2\)H\(^+\). However, we do not recommend to use it for the determination of hyperfine collisional data, since

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**FIG. 2.** Comparison between HCl–ortho-H\(_2\)(\(J_2 = 1\)) recoupling and IOS hyperfine cross sections for all the de-excitation transitions up to \(J_1 = 5\) at four different collisional energies. The vertical axis represents the hyperfine IOS cross sections and the horizontal axis represents the corresponding hyperfine recoupling cross sections. The two dashed lines in each panel delimit the region where the cross sections differ by less than a factor of 3.
the IOS method is not expected to lead to accurate hyperfine structure resolved collisional data at typical interstellar temperatures.

Next, we compute hyperfine S-IOS cross sections and rate coefficients, which we then compare to results obtained from the recoupling approach. Figs. 3 and 4 show a comparison between hyperfine recoupling and hyperfine S-IOS cross sections for all the de-excitation transitions up to $j_1 = 5$ at four different collisional energies. The vertical axis represents the hyperfine S-IOS cross sections and the horizontal axis represents the corresponding hyperfine recoupling cross sections. The two dashed lines in each panel delimit the region where the cross sections differ by less than a factor of 3.

FIG. 3. Comparison between HCl–para-H$_2$($j_2 = 0$) recoupling and S-IOS hyperfine cross sections for all the de-excitation transitions up to $j_1 = 5$ at four different collisional energies. The vertical axis represents the hyperfine S-IOS cross sections and the horizontal axis represents the corresponding hyperfine recoupling cross sections. The two dashed lines in each panel delimit the region where the cross sections differ by less than a factor of 3.

The accuracy of the S-IOS approach for collisions with ortho-H$_2$($j_2 = 1$), the agreement with the recoupling calculations only slightly improves when we use the S-IOS method instead of the IOS one. Thus, we do not recommend the S-IOS method to accurately evaluate the hyperfine cross sections and rate coefficients.

The accuracy of the S-IOS approach for collisions with para-H$_2$($j_2 = 0$) and not for collisions with ortho-H$_2$($j_2 = 1$) is at first surprising. However, one can see that in Eqs. (6) and (7), the computation of the fundamental cross sections is done regardless whether the colliding partner is ortho-H$_2$ or para-H$_2$. In contrast to heteronuclear diatomic molecules, H$_2$ exists in two nuclear-spin isomers that can be considered as separate species (orthoh–para-H$_2$ conversion is not possible through non-reactive collisions).

In an attempt to improve the accuracy of the S-IOS approach in the case of ortho-H$_2$ collisions, we replace the fundamental cross sections by the “fundamental” ones for ortho-H$_2$ collisions ($\sigma_{L_n}^{CC}L_{n+1/2,0}^{\pm}$) in Eqs. (6) and (7). We refer to this method as S-IOSb. Table 1 presents a comparison between recoupling, S-IOS and S-IOSb cross sections for a small sample of the case of collisions with ortho-H$_2$($j_2 = 1$).

Using S-IOSb method instead of S-IOS does not really improve the results. In both cases, the computation scales the
FIG. 4. Comparison between HCl–ortho-H\(_{2}\)\((j_1 = 1)\) recoupling and S-IOS hyperfine cross sections for all the de-excitation transitions up to \(j_1 = 5\) at four different collisional energies. The vertical axis represents the hyperfine S-IOS cross sections and the horizontal axis represents the corresponding hyperfine recoupling cross sections. The two dashed lines in each panel delimit the region where the cross sections differ by less than a factor of 3.

TABLE I. Comparison between selected HCl–ortho-H\(_{2}\)\((j_1 = 1)\) recoupling, S-IOS and S-IOSb hyperfine excitation cross sections (in \(\AA^2\)) at four different collisional energies. The percentage for the comparison are given by the following formula: \(\% = \frac{|S-IOS - Rec|}{Rec} \times 100\).
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hyperfine IOS cross sections by the ratio between $\sigma^\text{CC}_{h_1 h_2 \to j_1 j_2}$ and $\sigma^\text{IOS}_{h_1 h_2 \to j_1 j_2}$ and uses similar algebra, resulting in similar results using either the ortho- or the para-H$_2$ cross sections are used for fundamental cross sections.

Fig. 5 shows HCl–H$_2$ hyperfine recoupling and S-IOS rate coefficients for some selected transitions. The rate coefficients display the same features than the cross sections. A good agreement exists between recoupling and S-IOS results in the case of collisions with para-H$_2(j_2 = 0)$. This agreement improves with increasing temperatures. On the other hand, the agreement is very moderate for collisions with ortho-H$_2(j_2 = 1)$. Using the S-IOS approach cannot provide results with an accuracy better than a factor of 3-5.

To conclude on the methods comparison, we find that hyperfine S-IOS cross sections are in reasonable agreement with the recoupling crossing sections in the case of collisions with para-H$_2(j_2 = 0)$, especially for high kinetic energies/temperatures, while hyperfine S-IOS cross sections disagree with the recoupling crossing sections in the case of collisions with ortho-H$_2(j_2 = 1)$, regardless of the use of para- or ortho-H$_2$ fundamental cross sections.

We thus suggest that the S-IOS approximation should be used to compute hyperfine structure resolved cross sections at moderate and high collisional energies when S-matrices are not saved and when dealing only with para-H$_2(j_2 = 0)$ colliding partner. In the absence of nuclear spin free S-matrices, S-IOS approach may also be used for collisions with ortho-H$_2(j_2 = 1)$, but more caution should be taken about the accuracy of the results in this case. Accurate results at low energies/temperatures, while hyperfine S-IOS cross sections are in good agreement exists between recoupling and S-IOS results.

The hyperfine rate coefficients computed in this paper are the first of this kind for the HCl–H$_2$ collisional system. It is then interesting to also discuss the propensity rules of these new HCl–H$_2$ rate coefficients. First, we can retrieve the dominance of the transitions due to H$_2(j_2 = 1)$ collisions over the transitions due to H$_2(j_2 = 0)$ collisions, as previously observed for the purely rotational cross sections. Second, we can also observe the typical trend in favor of the transitions involving $\Delta j_1 = \Delta F_1$ for both para and ortho-H$_2$.

IV. SUMMARY AND DISCUSSION

In this paper, we have investigated the computation of hyperfine structure resolved cross sections and rate coefficients for the collisions of two diatomic molecules. Three collisional data sets (recoupling, IOS and S-IOS) for the HCl–H$_2$ collisional system have been compared in detail using both para-H$_2(j_2 = 0)$ and ortho-H$_2(j_2 = 1)$ colliding partners. S-IOS approximation was found to reproduce the recoupling results within a factor of 2 or better in the case of collisions with para-H$_2(j_2 = 0)$ and at intermediate and high kinetic energies while the two approximations fail in the case of collisions with ortho-H$_2(j_2 = 1)$.

HCl molecule is not very suitable for the use of IOS based methods as it is a light hydride. Hence, we can expect that the S-IOS approach may be in even better agreement with recoupling approach when considering heavier molecules such as HCN or HNC molecules. Rotational cross sections are available for these molecules, which will be good candidates for exploring the use of the S-IOS method.

It should be noted that the present theoretical approach can also be used to deal with fine structure of $^2\Sigma$ or $^3\Sigma$ electronic state molecules, as soon as the fine structure splitting is moderate. Indeed, fine structure resolved transitions could be obtained from rotationally resolved collisional data as it was recently done by Kalugina et al. in the case of CN–H$_2$ collisions.

Finally, this study provides the first hyperfine HCl–H$_2$ rate coefficients. Such data are crucial to interpret the recent spectra obtained from the Herschel telescope. The analysis of these emission spectra using the present collisional data will provide the astronomers with a better insight into the HCl abundance in the interstellar medium. Accurate determination of the HCl abundance in molecular clouds will also allow a better understanding of the interstellar chlorine chemistry, which is presently still an open question.

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