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# Depolarization rates of resonance lines of Mg, Ca, Sr and Na atoms by collisions with neutral hydrogen

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**Abstract.** Multipole relaxation and transfer rates due to isotropic collisions with neutral hydrogen atoms are calculated and a general expression for the hyperfine-structured levels are obtained. Evaluation of these rates has been carried out using accurate potential energy curves. The formulae given here for the depolarizing collisional rates should be useful for accurately modelling the complex linear polarization pattern of the Na i doublet in a complement to the ground state's depolarizing collisional rates which were presented in a previous paper (Kerkeni et al. 2000) hereafter referred to as Paper I. Similarly the depolarizing collisional rates of the Mg i, Ca i, Sr i resonance lines should be useful for polarization studies.

**Key words.** line: formation – polarization – atomic processes – Sun: atmosphere

## 1. Introduction

Recent observations of scattering polarization on the Sun have revealed the existence of "enigmatic" linear polarization signals in several spectral lines, which have motivated new theoretical investigations on atomic polarization and the Hanle effect (see e.g., the recent reviews by Trujillo Bueno 1999; 2001). Probably the most popular observational example is the case of the $D_1$ and $D_2$ lines of Na i (see Stenflo & Keller 1997). Soon after the publication of such "enigmatic" observations, Trujillo Bueno & Landi Degl'Innocenti (1997) showed, by means of selfconsistent radiative transfer calculations, that anisotropic radiation pumping processes in the solar atmosphere can lead to significant amounts of ground-level polarization, and to linear polarization signals in spectral lines with amplitudes in the observable range. In fact, Landi Degl'Innocenti (1998) could show, by adjusting of few free parameters, that a certain amount of ground-level atomic polarization in the hyperfine structure components of the ground level of sodium leads to a fairly good fit of the above-mentioned observations of linear polarization across the sodium doublet. More recently, Trujillo Bueno et al. (2002) have clarified the true physical origin of the ground-level polarization of Na i by carefully investigating, within the framework of the quantum theory of polarization, how it is actually produced, and modified by the action of a magnetic field of given strength and inclination.

Because isotropic collisions with the H atoms present in the stellar atmosphere contribute to depolarization of the atomic energy levels, a rigorous interpretation of the polarization spectra is possible only if the effects of the depolarizing collisions predominantly with H atoms are well understood for the spectral lines under consideration. In this paper we give the elastic and inelastic collisional rates of interest for the interpretation of the Na i, Mg i, Ca i, and Sr i resonance lines. Section 2 gives a brief introductory overview to familiarize the reader with the basic theoretical concepts and techniques applied for the computation of depolarizing rates caused by collisions with H atoms. Section 3 discusses the potential energy curves, while Sect. 4 focuses on the details of the applied theory. Finally, we show the results in Sect. 5, and summarize our main conclusions in Sect. 6.

## 2. Theoretical concepts and techniques

Nowadays evaluating potential energy curves is the only obstacle to overcome to perform collisional calculations. Obtaining accurate values of these potential energy curves yield reliable relaxation parameters. The potential energy curves presented here have been calculated in the Born-Oppenheimer approximation (Born & Oppenheimer 1927) and obtained by methods of quantum chemistry (Schaeffer 1977; Jensen 1999). The electronic Schrödinger equation was solved by variational techniques for each internuclear distance giving the electronic energies as eigenvalues. The electronic wave function was obtained by using state average MultiConfiguration Self Consistent Field (MCSCF) method (Werner & Knowles 1985, 1988) which is a natural extension of the one-configuration Self Consistent Field (SCF) method.

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At the SCF level, the electronic wave function is an antisymmetrical product of orbitals and electron spin functions and is given by a single determinant (Slater determinant) or configuration. Molecular orbitals that describe the wave function of each electron are determined by the field of the nuclei and the field arising from the average distribution of all the electrons. They are expanded in terms of atomic orbitals (LCAO method) built from a set of Gaussian functions (Boys 1950) in order to facilitate numerical integration. Optimization of the expansion coefficients for each internuclear distance is obtained by minimization of the energy of the electronic state. SCF wave functions give poor value for the relative energies, particularly for large internuclear distances.

To obtain a better accuracy, one must go beyond the SCF level. This can be done by using MCSCF wave functions given by a linear combination of determinants (configurations) built on a set of spinorbitals possibly larger than the set of orbitals occupied in the SCF configuration. Molecular orbitals as well as coefficients of the determinants are optimized at each internuclear distance. This MCSCF approach takes into account a large part of the correlation energy between electrons. In the case of very shallow potential energy curves (like Π states of NaH), the more accurate MultiReference Configuration Interaction method (MRCI) that includes all the single and double excitations from the MCSCF wave function is used. All the results were obtained using the MOLPRO package[1].

## 3. Ab initio potential for the MgH, SrH and NaH systems

Depolarization studies of Mg i, Ca i and Sr i resonance lines involve the excited $^1$P state only, the ground state $^1$S being unaffected by depolarizing collisions (because calcium has nuclear spin $I = 0$). However, this is not strictly true for Mg i and Sr i but it may be a sufficiently good approximation because their most abundant isotope have indeed $I = 0$; i.e. 90% for Mg i and 93% for Sr i. Concerning the Na i D lines, collisional depolarization occurs both in the ground state (3s $^2S_{1/2}$) and in the excited states (3p $^2P_{1/2}$ and 3p $^2P_{3/2}$). Results have been published for the ground state (see Paper I).

For CaH, accurate ab initio potential energy curves were available (Chambaud & Lévy 1989).

For MgH, the relevant potential energy curves are the third $^2\Sigma^+$ and second $^2\Pi$ states dissociating to the Mg(3s3p $^1$P) + H($^2$S) limit at large internuclear distances (taking into account the ground state $X^2\Sigma^+$ and an intermediate asymptote involving the Mg i atom in a triplet state (3s3p$^3$P). The Gaussian basis set for the H atom comprised the (8s, 4p, 3d) set of Widmark et al. (1990) contracted to [4s, 3p, 2d]. For magnesium, the basis comprised the (14s, 10p) functions of Sadlej & Urban (1991) and the (5d, 4f) functions of Widmark et al. (1991) contracted to [7s, 5p, 4d, 3f]. The total number of contracted Gaussian functions was 86. The potential energy curves were calculated from state average MCSCF wave functions in the ($4\sigma - 9\sigma, 2\pi - 4\pi, 1\delta$) active space.

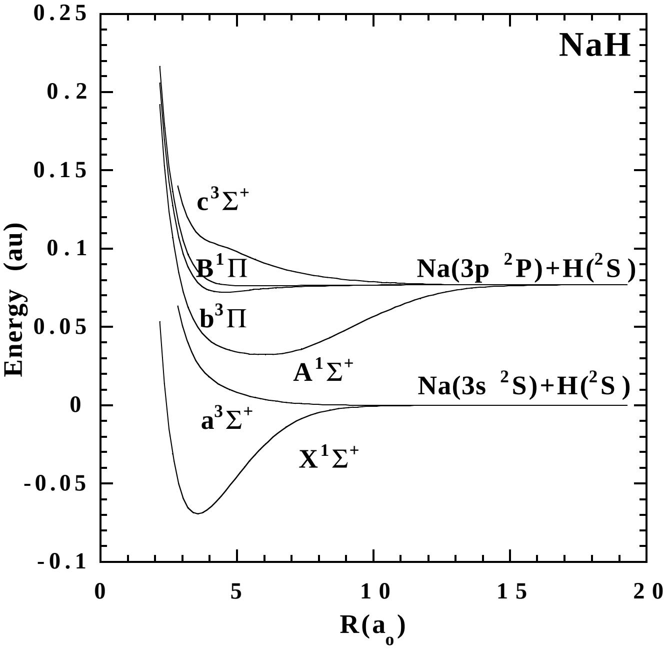

**Fig. 1.** Potential energy curves for NaH.

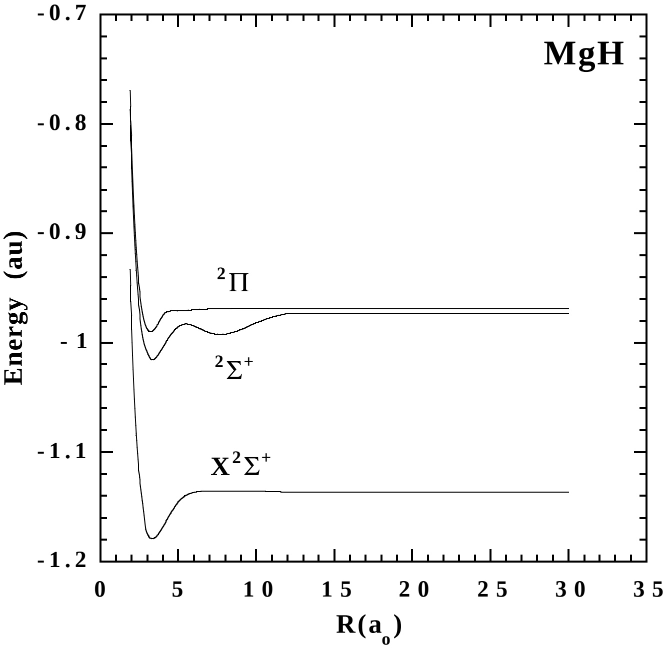

**Fig. 2.** Potential energy curves for MgH.

For SrH, the potential energy curves of interest are the $^2\Sigma^+$ and $^2\Pi$ states dissociating to the Sr(5s5p $^1$P)+H($^2$S) asymptote. This requires calculating five $^2\Sigma^+$ and four $^2\Pi$ states due to the first asymptotes involving the Sr i atom in $^1$S, $^1$D, $^3$P and $^3$D states. The Gaussian basis set for the H atom comprised the (7s, 4p, 3d, 2f) of Kendall et al. (1992) contracted to [5s, 4p]. For the Sr i atom, the basis includes the (11s, 15p, 10d, 6f) of Sadlej & Urban (1991) contracted to [4s, 9p, 4d]. The potential

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[1] MOLPRO is a package of ab initio programs written by H.-J. Werner and P. J. Knowles, with contributions from J. Almlöf, R. D. Amos, A. Berning, M. J. O. Deegan, F. Eckert, S. T. Elbert, C. Hampel, R. Lindh, W. Meyer, A. Nicklass, K. Peterson, R. Pitzer, A. J. Stone, P. R. Taylor, M. E. Mura, P. Pulay, M. Schuetz, H. Stoll, T. Thorsteinsson, and D. L. Cooper

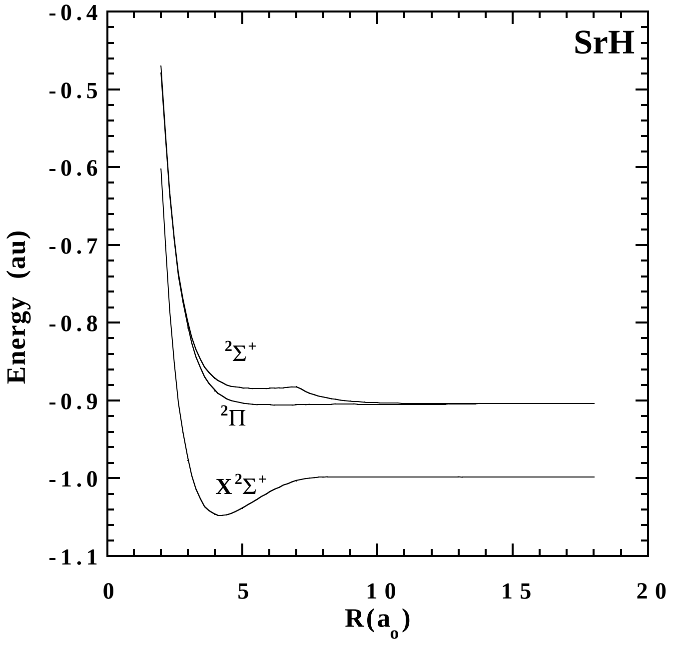

**Fig. 3.** Potential energy curves for SrH.

energy curves were calculated from MCSCF wave functions in the $(8\sigma - 14\sigma, 4\pi - 6\pi, 2\delta)$ active space.

Adiabatic potential energy curves for NaH have been determined using MRCI wave functions. The basis sets and active space used in these calculations are described in Paper I. The calculations concern the $X^1\Sigma^+$ and $a^3\Sigma^+$ states dissociating to the Na(3s $^2$S) + H($^2$S) asymptote and the $A^1\Sigma^+$,$B^1\Pi$,$b^3\Pi$ and $c^3\Sigma^+$ states dissociating to the Na(3p $^2$P) + H($^2$S) asymptote.

The results for the three systems are presented in Figs. 1, 2 and 3. The main characteristics of these potential energy curves is the presence of a large well in the $^1\Sigma^+$ states due to the ionic configuration $M^+H^-$ ($M^+ \equiv Mg^+,Sr^+,Na^+$).

In order to test the basis set and the active space, the minima $R_e$ of the attractive $X^1\Sigma^+$,$A^1\Sigma^+$,$b^3\Pi$ states were determined for the well studied NaH system (see Sachs et al. 1975; Pesl et al. 2000; Leininger et al. 2000). A fit of the first vibrational levels gives the harmonic frequency $\omega_e$. The vibrational levels were obtained from numerical integration of the radial Schrödinger equation using the Numerov method. The calculated values of these spectroscopic constants are given in Table 1 for comparison with the experimental and theoretical results. Our constants agree well with the experiments and improve some of the available theoretical results.

## 4. Dynamics

### 4.1. Close coupling equations

The potential energy curves described above were used to compute relaxation and transfer cross sections. Fully quantal close-coupling studies of the neutral systems Na-H, Mg-H, Ca-H ans Sr-H were performed using the formulation given by Mies (1973) and generalized by Launay & Roueff (1977).

The radiating atom with angular momentum $J$ collides with an H atom with angular momentum $j_2$. We couple $J$ and $j_2$ to obtain the total angular momentum $j$ of the two atoms. Owing to the invariance of the interaction potential $V$ under rotations of the total system, the total angular momentum $J^T = j + \ell$ and its space fixed projection $M^T$ are conserved during the collision. It is convenient to use scattering channel states $|J j_2 j \ell J^T\rangle$ which describe the asymptotic fragments with relative angular momentum $\ell$. The total wave function is expanded in terms of these channel states, the expansion coefficients are the radial amplitudes $F^{J^T}_{J' j_2 j' \ell', J j_2 j \ell}$ which satisfy the usual coupled radial equations (Spielfiedel et al. 1991). This set of equations is always decoupled into two blocks as a result of parity conservation. In the calculations, we have assumed that the H atom remains in its ground $^2$S state ($L_2 = 0, j_2 = 1/2$) and we have neglected collision-induced quenching to the other L states of the radiating atom. The scattering equations were solved subject to boundary conditions which define the T-matrix elements (Spielfiedel et al. 1991). The numerical method used is the Log Derivative Method (Johnson 1977). Convergence was checked in terms of the range and step size in the scattering coordinate in the radial equations.

### 4.2. General expression of the relaxation constants and of the transfer rates

Under typical conditions of formation of strong resonance lines in stellar atmospheres, the interaction of the radiating atomic system with the perturbing gas is given by the relaxation matrix (Fano 1963). Under the assumption that the impact approximation is valid, the relaxation matrix $\hat{G}$ is frequency independent and can be expressed in terms of collisional amplitudes (Nienhuis 1976) or collision T-matrix elements (Fano 1963). As the internal state distribution of the perturbers and the distribution of relative velocities are isotropic, the collisional relaxation of the atomic density matrix $\rho$ is fully isotropic. As a consequence, the relaxation matrix $\hat{G}$ is considerably simplified by using an expansion in components $T^\kappa_q$ of irreducible tensorial sets (Fano 1949, 1954, 1957; Omont 1977; Blum 1981). We use here the same notations as in Paper I.

Due to the isotropy of the collisional relaxation, only the multipole components with the same value of $\kappa$ and $q$ are coupled, and the relaxation rate constants are $q$ independent. Hence the relaxation equations may be written as:

$$\left(\frac{\mathrm{d}\rho^\kappa_q(\lambda J)}{\mathrm{d}t}\right)_{\mathrm{rel}} = -g^\kappa(\lambda J)\rho^\kappa_q(\lambda J) + \sum_{J' \neq J} g^\kappa(\lambda J, \lambda' J')\, \rho^\kappa_q(\lambda' J'). \quad (1)$$

In this equation, the coefficients $g^\kappa(\lambda J, \lambda' J')$ express the variation of the density matrix element $\rho^\kappa_q$ of the atomic state $\lambda J$ in terms of the density matrix elements $\rho^\kappa_q$ of all the states $\lambda' J'$.

For $J \neq J'$, $g^\kappa(\lambda J, \lambda' J')$ corresponds to collisional transfer of population ($\kappa = 0$), orientation ($\kappa = 1$) and alignment ($\kappa = 2$) from state $J'$ to state $J$.

$$g^\kappa(\lambda J, \lambda' J') = n_{\mathrm{H}} \int_0^\infty v f(v) \mathrm{d}v \sigma^\kappa(J' \to J) \quad (2)$$

**Table 1.** Calculated and experimental spectroscopic constants for the $X^1\Sigma^+$, $A^1\Sigma^+$ and $b^3\Pi$ states of $^{23}Na^1H$.

| State | Reference | $R_e$ ($a_0$) | $\omega_e$ (cm$^{-1}$) | $B_e$(cm$^{-1}$) | $\alpha_e$(cm$^{-1}$) | $D_e$(eV) | $T_e$(cm$^{-1}$) |
|---|---|---|---|---|---|---|---|
| $X^1\Sigma^+$ | this work | 3.57 | 1166.7 | 4.909 | 0.149 | 1.89 | 0 |
| | (Sachs et al. 1975) | 3.61 | – | – | 0.135 | 1.878 | 0 |
| | (Meyer & Rosmus 1975) | 3.57 | 1172.3 | 4.88 | 0.132 | 1.92 | 0 |
| | (Huber & Herzberg 1979) | 3.57 | 1171.4 | 4.902 | – | 2.12 | 0 |
| | (Olson & Liu 1980) | 3.558 | 1171.8 | 4.927 | – | 1.922 | 0 |
| | (Orth et al. 1980) | 3.566 | 1171.4 | 4.902 | 0.1386 | – | 0 |
| | (Pesl et al. 2000) | – | 1171.968 | 4.90327 | 0.137 | – | 0 |
| $A^1\Sigma^+$ | this work | 6.05 | 313.01 | 1.7362 | −0.0679 | 1.21 | 22 310 |
| | (Sachs et al. 1975) | 6.19 | – | – | – | 1.203 | 22 122 |
| | (Olson & Liu 1980) | 5.992 | 320 | 1.735 | – | 1.239 | 22 568 |
| | (Huber & Herzberg 1979) | 6.062 | – | – | – | 1.41 | 22 719 |
| | (Orth et al. 1980) | 6.0346 | 317.56 | 1.712 | −0.09152 | – | 22 713 |
| | (Pesl et al. 2000) | – | 319.96 | 1.70553 | −0.0971 | – | – |
| $b^3\Pi$ | this work | 4.46 | 419.88 | 3.0402 | 0.239 | 0.13 | 31 044 |
| | (Sachs et al. 1975) | 4.46 | 419.39 | 3.533 | 0.853 | 0.109 | 30 938 |
| | (Olson & Liu 1980) | 4.497 | 430.3 | 3.09 | – | 0.133 | 31 479 |
| | (Huber & Herzberg 1979) | 4.195 | 419 | – | – | – | 30 940 |

with

$$\sigma^{\kappa}(J' \to J) = \sum_m (-1)^{J+J'+\kappa+m}(2m+1) \times \begin{Bmatrix} J' & J' & \kappa \\ J & J & m \end{Bmatrix} B(JJ',m) \tag{3}$$

and

$$B(JJ';m) = \frac{\pi}{(2j_2+1)k_{J'}^2} \sum_{j_b j_{b'} \ell \ell'} (2j_b+1)(2j_{b'}+1) \times \Big| \sum_{J^{\mathrm{T}} j j'} \sqrt{(2j+1)(2j'+1)}(-1)^{J+j_2+J^{\mathrm{T}}} \begin{Bmatrix} J & j_2 & j \\ \ell & J^{\mathrm{T}} & j_b \end{Bmatrix} \times \begin{Bmatrix} J' & j_2 & j' \\ \ell' & J^{\mathrm{T}} & j_{b'} \end{Bmatrix} \begin{Bmatrix} J & J' & m \\ j_b' & j_b & J^{\mathrm{T}} \end{Bmatrix} \langle J' j_2 j' \ell' J^{\mathrm{T}} | T | J j_2 j \ell J^{\mathrm{T}} \rangle \Big|^2. \tag{4}$$

In Eq. (2) $f(v)$ is the Maxwellian distribution of relative velocities $v$ at temperature $T$ and coefficients $B$ are a generalization of the Grawert factors introduced by Reid (1973). Here, $\mu$ is the reduced mass and $k_{J'}$ is the wavenumber defined by $k_{J'}^2 = 2\mu(E - E_{J'})$, where $E$ and $E_{J'}$ are respectively the total and fine structure energies.

For $J = J'$:

$$g^{\kappa}(J) = n_{\mathrm{H}} \int_0^{\infty} v f(v) \mathrm{d}v \sigma^{\kappa}(J). \tag{5}$$

The relaxation cross section $\sigma^{\kappa}(J)$ is the sum of two terms $\Lambda^{\kappa}(J)$ and the fine structure transfer cross section $\sum_{J' \neq J} \sigma(J \to J')$:

$$\sigma^{\kappa}(J) = \Lambda^{\kappa}(J) + \sum_{J' \neq J} \sigma(J \to J') \tag{6}$$

with

$$\Lambda^{\kappa}(J) = \sum_m \frac{2m+1}{2J+1}[1 - (-1)^{2J+\kappa+m}(2J+1) \times \begin{Bmatrix} m & J & J \\ \kappa & J & J \end{Bmatrix}] B(JJ;m) \tag{7}$$

and

$$\sigma(J \to J') = \frac{\pi}{k_J^2} \sum_{J^{\mathrm{T}} j j' \ell \ell'} \frac{2J^{\mathrm{T}}+1}{(2J+1)(2j_2+1)} \times |\langle J' j_2 j' \ell' J^{\mathrm{T}} | T | J j_2 j \ell J^{\mathrm{T}} \rangle|^2. \tag{8}$$

Calculation of all cross sections was carried out for a range of energies sampled in a Maxwellian distribution from 200 K to 80 000 K. Convergence as function of $J^{\mathrm{T}}$ and of the step in the Maxwellian integration over speed was carefully checked.

## 5. Results

### 5.1. Depolarization constants of the $^1P$ excited state of Mg I, Ca I and Sr I

Alkali earth atoms in a $^1$P state have an electronic angular momentum $L = 1$ and an electronic spin $S = 0$, so the angular momentum of the radiating atom is $J = 1$. Combining $J$ with the angular momentum $j_2 = 1/2$ of the H atom, we obtain the total angular momentum $j = 1/2, 3/2$. The relevant channels for a total angular momentum $J^{\mathrm{T}}$ are given in Appendix A. So, for each kinetic energy, two sets of three-channel scattering equations were solved for a given value of the total angular momentum $J^{\mathrm{T}}$ ranging from 1.5 to some suitable large value

(up to 700.5 at the highest energies) in order to obtain convergence of the summation.
As inelastic cross sections to other states are negligible, we have only to consider the collisional relaxation rates of rank 0, 1 and 2. The corresponding cross sections are given by:

$$\begin{aligned}\sigma^0(1) &= 0\\ \sigma^1(1) &= \frac{1}{2}B(11;1)+\frac{5}{2}B(11;2)\\ \sigma^2(1) &= \frac{3}{2}B(11;1)+\frac{3}{2}B(11;2).\end{aligned} \tag{9}$$

Coefficients $g^\kappa$ are presented in Figs. 4, 5 and 6. As expected, we find similarities in the three systems: all the rates increase smoothly with temperature and in all cases, the relaxation rate of orientation $g^1$ is larger than the relaxation rate of alignment $g^2$. As the reduced masses of the three systems are close, one may conclude that the relative differences between the results are due to the differences in the interaction potential energy curves, reflecting essentially the relative atomic sizes.

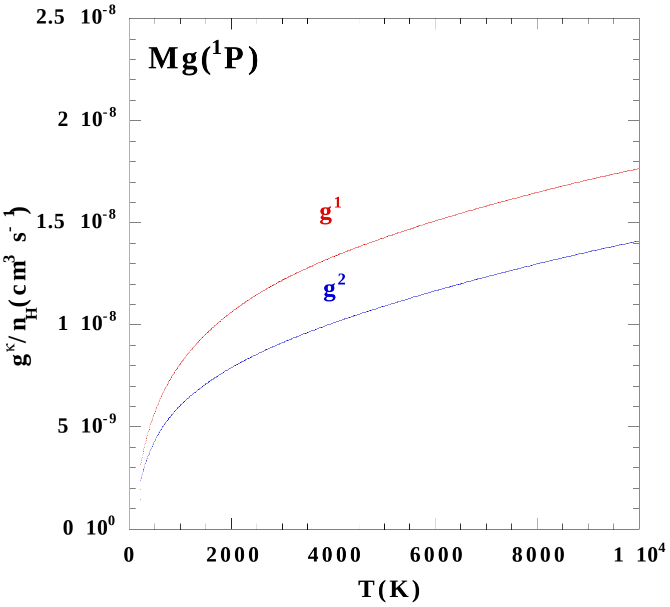

**Fig. 4.** Relaxation rates $g^1/n_{\rm H}({\rm cm}^3\,{\rm s}^{-1})$ and $g^2/n_{\rm H}({\rm cm}^3\,{\rm s}^{-1})$ versus temperature $T$(K).

### 5.2. Collisional relaxation and transfer rates in the Na $^2P_{1/2}$ and $^2P_{3/2}$ excited states

The excited $^2$P$_J$ states of the Na I atom correspond to an electronic angular momentum $L = 1$ and an electronic spin $S = 1/2$, so that the total electronic angular momentum is $J = 1/2$ or $J = 3/2$. For each energy, two sets of six coupled equations of the radiating atom (see Appendix B for the definition of the collisional channels) were solved for a total angular momentum $J^{\rm T}$ ranging from a minimum value equal to 2 (due to a condition of non negative $\ell$ value, see also Appendix B) to a large value (up to 700) insuring negligible contributions of larger $J^{\rm T}$ values.

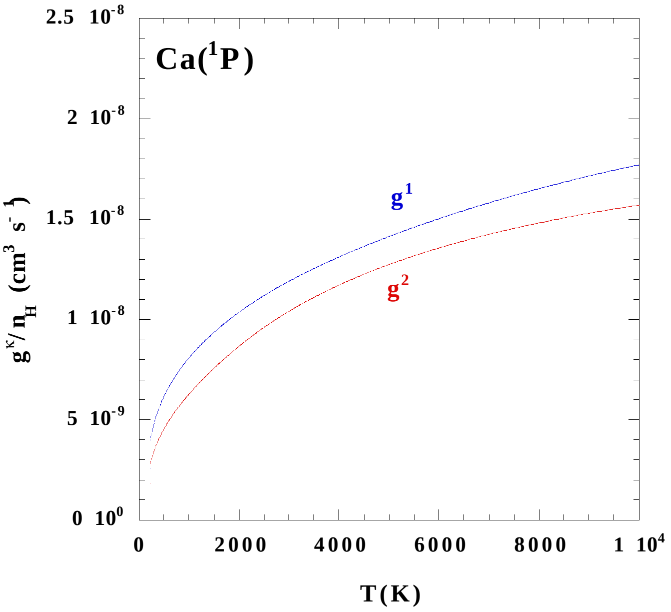

**Fig. 5.** Relaxation rates $g^1/n_{\rm H}({\rm cm}^3\,{\rm s}^{-1})$ and $g^2/n_{\rm H}({\rm cm}^3\,{\rm s}^{-1})$ versus temperature $T$(K).

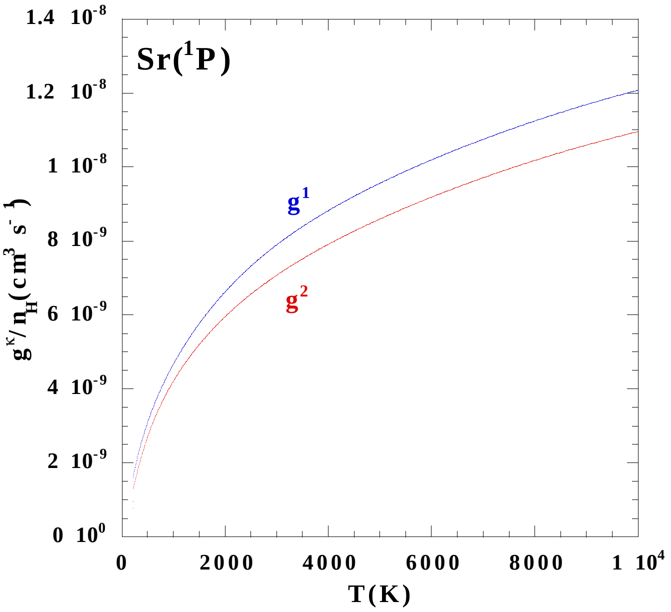

**Fig. 6.** Relaxation rates $g^1/n_{\rm H}({\rm cm}^3\,{\rm s}^{-1})$ and $g^2/n_{\rm H}({\rm cm}^3\,{\rm s}^{-1})$ as function of temperature $T$(K).

We give here the explicit expressions of the $\Lambda^\kappa$ in terms of the Grawert coefficients $B$ were given by Reid (1973) for $J = 1/2$ and $J = 3/2$.

Explicit expressions of the tensorial tranfer cross sections between $J = 1/2$ and $J = 3/2$ states are the following:

$$\begin{aligned}\sigma^0\left(\frac{3}{2}\rightarrow\frac{1}{2}\right) &= \frac{1}{2\sqrt{2}}\left[3B\left(\frac{1}{2}\frac{3}{2};1\right)+5B\left(\frac{1}{2}\frac{3}{2};2\right)\right]\\ \sigma^1\left(\frac{3}{2}\rightarrow\frac{1}{2}\right) &= \sigma^1\left(\frac{1}{2}\rightarrow\frac{3}{2}\right)=\frac{\sqrt{10}}{4}\left[B\left(\frac{1}{2}\frac{3}{2};1\right)-B\left(\frac{1}{2}\frac{3}{2};2\right)\right]\\ \sigma^2\left(\frac{3}{2}\rightarrow\frac{1}{2}\right) &= \sigma^2\left(\frac{1}{2}\rightarrow\frac{3}{2}\right)=0.\end{aligned} \tag{10}$$

The usual fine structure transfer cross section is:

$$\sigma\left(\frac{1}{2}\rightarrow\frac{3}{2}\right)=\frac{5}{2}B\left(\frac{1}{2}\frac{3}{2};2\right)+\frac{3}{2}B\left(\frac{1}{2}\frac{3}{2};1\right) \tag{11}$$

and is thus proportional to $\sigma^0\left(\frac{3}{2}\rightarrow\frac{1}{2}\right)\cdot$

The calculated relaxation rates, polarization transfer rates and fine structure transfer rate are presented in Figs. 7, 8 and 9. All these rates increase slowly with the temperature. As mentioned previously, the relaxation rates are larger than the transfer rates, the polarization transfer rate $g^1(1/2,3/2)$ being almost negligible in comparison with the $g^\kappa(1/2)$ and $g^\kappa(3/2)$ coefficients. We remark that the differences between $g^1(1/2)$ and $g^3(3/2)$ are nowhere discernible to the resolution of the figure, this results from compensation of the two components of the relaxation cross sections (see Eq. (6)). The same trend was obtained by Wilson & Shimoni (1975) for Na(3p $^2$P) – He collisions. Table 2 shows a comparison of our calculated fine structure rate with previous results. We note a significant difference in these values due to the different potential energy curves used, nevertheless our values are very similar to those obtained by Monteiro et al. 1985 from potential energy curves that include correctly the ionic configuration in the $^1\Sigma^+$ molecular states. This indicates the importance of an accurate description of the potential energy curves in the intermediate and large internuclear distances.

### 5.3. *Relaxation among the hyperfine levels of the Na atom*

The generalization of Eq. (2) with $J = J'$ to include the effects of nuclear spin has been studied by (Omont 1977). We consider the case of a single hyperfine multiplet, with electronic angular momentum $J$ and with nuclear spin $I$. The total angular momentum $F$ takes the values $F = \mid J-I\mid, \mid J-I\mid +1, ..., J+I$ and we may consider possible off diagonal elements of the corresponding density matrix. The density matrix $\hat{\rho}$ can be expanded as (Omont 1977):

$$\hat{\rho}=\sum_{FF'}\sum_{KQ}\rho^K_Q(FF')\,T^K_Q(FF')^\dagger. \tag{12}$$

Where

$$\begin{aligned}T^K_Q(FF') &= \sum_{M_F}(-1)^{F-M_F}(2K+1)^{1/2}\\ &\times\begin{pmatrix}F & F' & K\\ M_F & -M'_F & -Q\end{pmatrix}\mid FM_F\rangle\langle F'M'_F\mid\end{aligned} \tag{13}$$

() is a $3j$-coefficient (Fano & Racah 1959; Brink & Satchler 1962).

The density matrix for the electronic states can be expanded in terms of the tensors $T^{\kappa_J}_{q_J}$ $(0\le\kappa_J\le 2J)$ and the density matrix for the nuclear states have the tensors $T^{\kappa_I}_{q_I}$ $(0\le\kappa_I\le 2I)$ as a basis.

The unitary transformation from the basis $T^K_Q(FF')$ to the basis $T^{\kappa_J}_{q_J}\otimes T^{\kappa_I}_{q_I}$ is given by:

$$\begin{aligned}T^K_Q(FF') &= \sum_{\kappa_J q_J}\sum_{\kappa_I q_I}(-1)^{\kappa_J-\kappa_I-Q}[(2F+1)(2F'+1)]^{1/2}\\ &\times[(2\kappa_J+1)(2\kappa_I+1)(2K+1)]^{1/2}\\ &\times\begin{pmatrix}\kappa_J & \kappa_I & K\\ q_J & q_I & -Q\end{pmatrix}\begin{Bmatrix}J & I & F\\ J & I & F'\\ \kappa_J & \kappa_I & K\end{Bmatrix}T^{\kappa_J}_{q_J}T^{\kappa_I}_{q_I}\end{aligned} \tag{14}$$

where {} denotes a Wigner $9j$-coefficient (Fano & Racah 1959; Brink & Satchler 1962). As mentionned by Omont (1977), collisions are brief enough for the hyperfine coupling to be neglected. Then the collision S-matrix is just the direct product of the identity in the nuclear spin space and the collision matrix relative to the electronic coordinates computed in the absence of nuclear spin (see Paper I).

As the relaxation matrix is known in the "uncoupled" basis $T^{\kappa_J}_{q_J}(JJ)T^{\kappa_I}_{q_I}(II)$, in the case of an electronic multiplet $\{\lambda J\}$ we obtain the new matrix in the "coupled" basis $T^{(K)}_Q((JI)F,(JI)F')$ from the following unitary transformations:

$$\begin{aligned}\rho^K_Q(F,F') &= \sum_{\kappa_J q_J}\sum_{\kappa_I q_I}(-1)^{\kappa_J-\kappa_I-Q}[(2\kappa_J+1)(2\kappa_I+1)]^{1/2}\\ &\times[(2K+1)(2F+1)(2F'+1)]^{1/2}\\ &\times\begin{pmatrix}\kappa_J & \kappa_I & K\\ q_J & q_I & -Q\end{pmatrix}\begin{Bmatrix}J & I & F\\ J & I & F'\\ \kappa_J & \kappa_I & K\end{Bmatrix}\rho^{\kappa_J}_{q_J}\rho^{\kappa_I}_{q_I}.\end{aligned} \tag{15}$$

The time variation due to collisional relaxation of the element $\rho^K_Q(FF')$ is given by:

$$\begin{aligned}\frac{\mathrm{d}[^{(\lambda J)}\rho^K_Q(FF')]}{\mathrm{d}t} &= -\sum_{F''F'''}G_K(FF',F''F''')[^{(\lambda J)}\rho^K_Q(F''F''')]\\ &+\sum_{F''F'''}\sum_{J'\neq J}Q_K(FF',F''F''')[^{(\lambda' J')}\rho^K_Q(F''F''')]\end{aligned} \tag{16}$$

where the relaxation rates $G_K$ are related to the electronic relaxation rate $g^{\kappa_J}(\lambda J)$ (Omont 1977):

$$\begin{aligned}&G_K(FF',F''F''') = [(2F+1)(2F'+1)]^{1/2}\\ &\times[(2F''+1)(2F'''+1)]^{1/2}\sum_{\kappa_J\kappa_I}(2\kappa_J+1)(2\kappa_I+1)\\ &\times\begin{Bmatrix}J & I & F\\ J & I & F'\\ \kappa_J & \kappa_I & K\end{Bmatrix}\begin{Bmatrix}J & I & F''\\ J & I & F'''\\ \kappa_J & \kappa_I & K\end{Bmatrix}g^{\kappa_J}(\lambda J).\end{aligned} \tag{17}$$

In the same way, we obtain transfer hyperfine rates pertaining to the electronic transfer rate $g^{\kappa_J}(\lambda J,\lambda' J')$:

$$\begin{aligned}&Q_K(FF',F''F''') = [(2F+1)(2F'+1)]^{1/2}\\ &\times[(2F''+1)(2F'''+1)]^{1/2}\sum_{\kappa_I\kappa_J}(2\kappa_J+1)(2\kappa_I+1)\\ &\times\begin{Bmatrix}J & I & F\\ J & I & F'\\ \kappa_J & \kappa_I & K\end{Bmatrix}\begin{Bmatrix}J' & I & F''\\ J' & I & F'''\\ \kappa_J & \kappa_I & K\end{Bmatrix}g^{\kappa_J}(\lambda J,\lambda' J').\end{aligned} \tag{18}$$

These expressions are useful for any atom with nuclear spin I. The nuclear spin of the Na atom is $I = 3/2$, which yields two

**Table 2.** Temperature-dependent fine structure rate $g(1/2 \rightarrow 3/2)$ of Na. The rates are in units of $10^{-9}$ cm$^3$ s$^{-1}$.

| $T$(K) | 4000 | 4500 | 5000 | 6000 | 7000 | 8000 | 9000 | 10 000 |
|---|---|---|---|---|---|---|---|---|
| This work | 7.45 | 8.87 | 8.26 | 8.93 | 9.49 | 9.95 | 10.33 | 10.65 |
| (Monteiro et al. 1985) | - | - | 8.06 | 8.62 | 9.16 | 9.7 | 10.04 | - |
| (Roueff 1974) | - | 5.12 | - | 5.61 | 5.95 | - | 6.45 | 6.75 |
| (Lewis et al. 1971) | - | - | 3.03 | - | - | - | - | - |

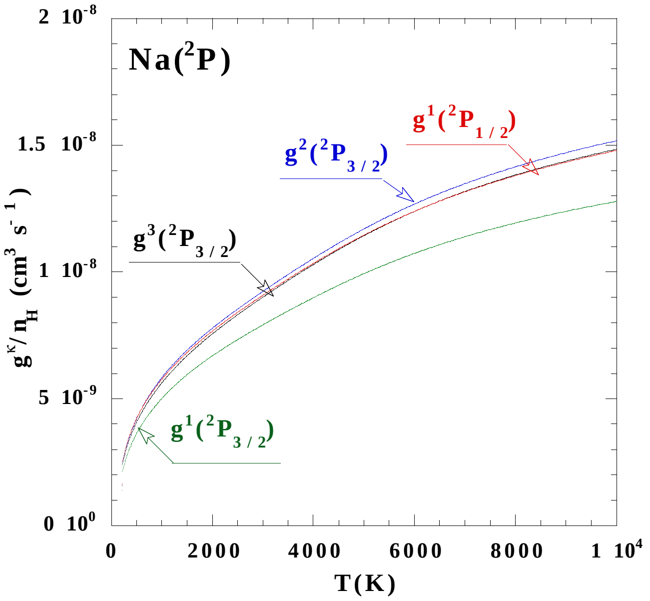

**Fig. 7.** Relaxation rates $g^1/n_{\mathrm{H}}$(cm$^3$ s$^{-1}$), $g^2/n_{\mathrm{H}}$(cm$^3$ s$^{-1}$) and $g^3/n_{\mathrm{H}}$(cm$^3$ s$^{-1}$) versus temperature $T$(K).

hyperfine levels in the $J = 1/2$ state, $F = 1$ and $F = 2$ and four hyperfine levels in the $J = 3/2$ state, $F = 0, 1, 2, 3$. We can apply Eqs. (2) and (5) to obtain the relaxation rates of the Zeeman multiplet and then deduce from Eqs. (17) and (18) all the relaxation rates between the hyperfine levels. Since there are many values and combinations of $F$ and $F'$, we give in Appendix C the values for ($F = F'$ and $K = 0, 2, 4$) related with the $G_K$ and $Q_K$ values.

As previously mentioned in the case of the multipole relaxation of the hyperfine levels in the ground state the algebra coefficients are a fraction of one and thus all the collisional rates among the excited hyperfine levels are of the same order of magnitude as the $g^\kappa$ coefficients of the fine structure $^2\mathrm{P}_{1/2}$ and $^2\mathrm{P}_{3/2}$ levels.

### *5.4. Analytical representation*

Cross sections were averaged over a Maxwell distribution of velocities. The variation of the relaxation rates with the temperature is very smooth and was found to increase as $T^\alpha$ and is given as follows for 200 K $\leq T \leq$ 10000 K.

Mg($^1$P) + H:

$$g^1 = 1.3836 \times 10^{-8} n_{\mathrm{H}} \left(\frac{T}{5000}\right)^{0.329} \quad (\mathrm{s}^{-1})$$
$$g^2 = 1.079 \times 10^{-8} n_{\mathrm{H}} \left(\frac{T}{5000}\right)^{0.367} \quad (\mathrm{s}^{-1}) \qquad (19)$$

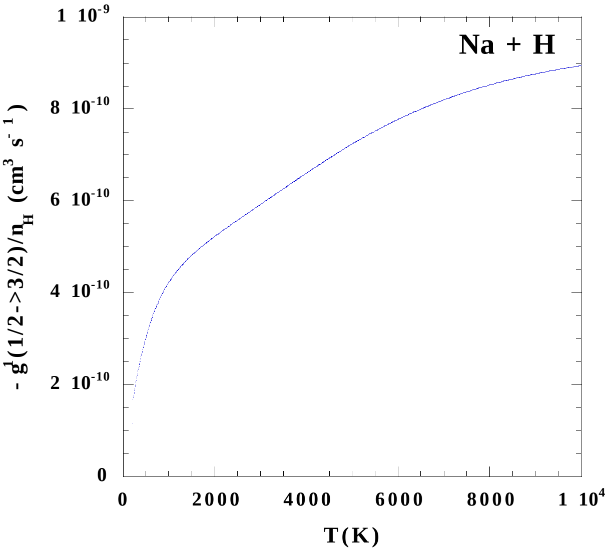

**Fig. 8.** Polarization transfer rate $g^1(3/2, 1/2)/n_{\mathrm{H}}$(cm$^3$ s$^{-1}$) as function of temperature $T$(K).

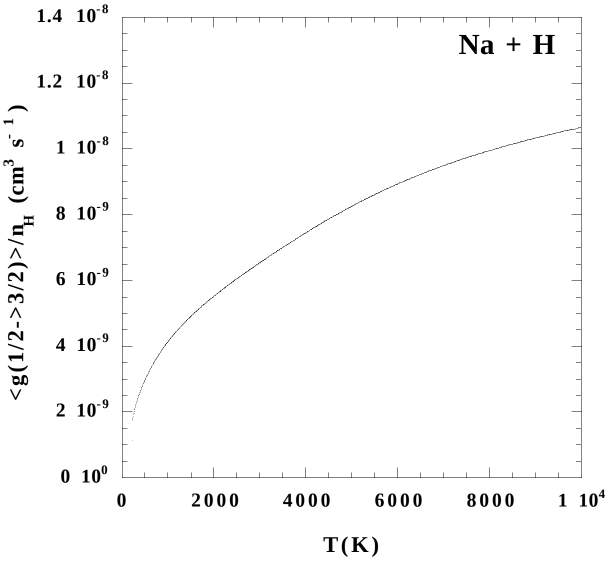

**Fig. 9.** fine structure rate versus temperature $T$(K).

Ca($^1$P)+H:

$$g^1 = 1.3826 \times 10^{-8} n_{\mathrm{H}} \left(\frac{T}{5000}\right)^{0.321} \quad (\mathrm{s}^{-1})$$
$$g^2 = 1.1861 \times 10^{-8} n_{\mathrm{H}} \left(\frac{T}{5000}\right)^{0.345} \quad (\mathrm{s}^{-1}) \qquad (20)$$

$\mathrm{Sr}(^1\mathrm{P}) + \mathrm{H}$:

$$\begin{aligned} g^1 &= 8.9875 \times 10^{-9} n_\mathrm{H} \left(\frac{T}{5000}\right)^{0.376} (\mathrm{s}^{-1}) \\ g^2 &= 8.0015 \times 10^{-9} n_\mathrm{H} \left(\frac{T}{5000}\right)^{0.386} (\mathrm{s}^{-1}) \end{aligned} \tag{21}$$

$\mathrm{Na}(^2\mathrm{P}) + \mathrm{H}$:

$$J = 1/2 \quad g^1 = 1.0914 \times 10^{-8} n_\mathrm{H} \left(\frac{T}{5000}\right)^{0.388} (\mathrm{s}^{-1}) \tag{22}$$

$$\begin{aligned} J = 3/2 \quad g^1 &= 9.5005 \times 10^{-9} n_\mathrm{H} \left(\frac{T}{5000}\right)^{0.377} (\mathrm{s}^{-1}) \\ g^2 &= 1.1183 \times 10^{-8} n_\mathrm{H} \left(\frac{T}{5000}\right)^{0.384} (\mathrm{s}^{-1}) \\ g^3 &= 1.1292 \times 10^{-8} n_\mathrm{H} \left(\frac{T}{5000}\right)^{0.442} (\mathrm{s}^{-1}) \end{aligned} \tag{23}$$

$$\begin{aligned} g^0(1/2 \rightarrow 3/2) &= g^0(3/2 \rightarrow 1/2) \\ &= 5.5685 \times 10^{-9} n_\mathrm{H} \left(\frac{T}{5000}\right)^{0.379} (\mathrm{s}^{-1}) \\ g(1/2 \rightarrow 3/2) &= 2 \times g(3/2 \rightarrow 1/2) \\ &= 7.8751 \times 10^{-9} n_\mathrm{H} \left(\frac{T}{5000}\right)^{0.379} (\mathrm{s}^{-1}) \\ g^1(1/2 \rightarrow 3/2) &= g^1(3/2 \rightarrow 1/2) \\ &= -0.6898 \times 10^{-9} n_\mathrm{H} \left(\frac{T}{5000}\right)^{0.302} (\mathrm{s}^{-1}). \end{aligned} \tag{24}$$

## 6. Conclusions

As mentioned in the introduction, the problem is to determine accurate relaxation rates by collision with H atoms. In the case of sodium, hyperfine rates should be useful for modelling the linear polarization observed in the center of the $D_2$ line (Kerkeni & Bommier 2002). Collisional depolarization in the upper level occurs if the rate is larger than the spontaneous emission coefficient $A$. Assuming $A \simeq 10^8$ s$^{-1}$, collisional depolarization in the upper state is complete if $G_2 \geq 10^8$ s$^{-1}$. As the $G_2$ coefficients are of the same order of magnitude as $g^\kappa$ coefficients, and assuming a temperature of 5000 K, we can conclude that the upper level is depolarized for hydrogen densities larger than ($10^{17}$ cm$^{-3}$).

As previously mentioned (see Paper I), depolarization in the ground level occurs for much lower densities ($10^{14}$ cm$^{-3}$). Of course, the correct diagnostic requires the resolution of the rate equations including radiative and collisional processes between hyperfine levels. This work is in progress (Kerkeni & Bommier 2002).

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## Appendix A: Channels for a $^1$P state

| Parity | | $(-)^{J^\mathrm{T}-1/2}$ | | | | $(-)^{J^\mathrm{T}+1/2}$ |
|---|---|---|---|---|---|---|
| $J$ | $j$ | $\ell$ | channel number | $J$ | $j$ | $\ell$ |
| 1 | $\frac{1}{2}$ | $J^\mathrm{T} + 1/2$ | 1 | 1 | $\frac{1}{2}$ | $J^\mathrm{T} - 1/2$ |
| 1 | $\frac{3}{2}$ | $J^\mathrm{T} - 3/2$ | 2 | 1 | $\frac{3}{2}$ | $J^\mathrm{T} - 1/2$ |
| 1 | $\frac{3}{2}$ | $J^\mathrm{T} + 1/2$ | 3 | 1 | $\frac{3}{2}$ | $J^\mathrm{T} + 3/2$ |

## Appendix B: Channels for a $^2$P state

| Parity | | $(-)^{J^\mathrm{T}}$ | | | | $(-)^{J^\mathrm{T}+1}$ |
|---|---|---|---|---|---|---|
| $J$ | $j$ | $\ell$ | channel number | $J$ | $j$ | $\ell$ |
| $\frac{1}{2}$ | 1 | $J^\mathrm{T} - 1$ | 1 | $\frac{1}{2}$ | 0 | $J^\mathrm{T}$ |
| $\frac{1}{2}$ | 1 | $J^\mathrm{T} + 1$ | 2 | $\frac{1}{2}$ | 1 | $J^\mathrm{T}$ |
| $\frac{3}{2}$ | 1 | $J^\mathrm{T} - 1$ | 3 | $\frac{1}{2}$ | 1 | $J^\mathrm{T}$ |
| $\frac{3}{2}$ | 1 | $J^\mathrm{T} + 1$ | 4 | $\frac{1}{2}$ | 2 | $J^\mathrm{T} - 2$ |
| $\frac{3}{2}$ | 2 | $J^\mathrm{T} - 1$ | 5 | $\frac{1}{2}$ | 2 | $J^\mathrm{T}$ |
| $\frac{3}{2}$ | 2 | $J^\mathrm{T} + 1$ | 6 | $\frac{1}{2}$ | 2 | $J^\mathrm{T} + 2$ |

## Appendix C: Values of the hyperfine depolarizing rates

The variation of the hyperfine depolarizing rates with the temperature is very smooth and was found to increase as $T^\alpha$ and is given as follows for 200 K $\leq T \leq$ 10 000 K.

$$\begin{aligned} J = 1/2 \quad G_0(11,11) &= 0.6821 \times 10^{-8} n_\mathrm{H} \left(\frac{T}{5000}\right)^{0.388} (\mathrm{s}^{-1}) \\ G_2(11,11) &= 0.8867 \times 10^{-8} n_\mathrm{H} \left(\frac{T}{5000}\right)^{0.388} (\mathrm{s}^{-1}) \\ G_4(11,11) &= 0.0 (\mathrm{s}^{-1}) \\ G_0(22,22) &= 0.4093 \times 10^{-8} n_\mathrm{H} \left(\frac{T}{5000}\right)^{0.388} (\mathrm{s}^{-1}) \\ G_2(22,22) &= 0.6139 \times 10^{-8} n_\mathrm{H} \left(\frac{T}{5000}\right)^{0.388} (\mathrm{s}^{-1}) \\ G_4(22,22) &= 1.0914 \times 10^{-8} n_\mathrm{H} \left(\frac{T}{5000}\right)^{0.388} (\mathrm{s}^{-1}) \end{aligned} \tag{C.1}$$

$$\begin{aligned} J = 3/2 \quad G_0(00,00) &= 1.0128 \times 10^{-8} n_\mathrm{H} \left(\frac{T}{5000}\right)^{0.410} (\mathrm{s}^{-1}) \\ G_2(00,00) &= 0.0 (\mathrm{s}^{-1}) \\ G_4(00,00) &= 0.0 (\mathrm{s}^{-1}) \end{aligned}$$

$$G_0(11,11) = 8.6305\times 10^{-9} n_\mathrm{H}\left(\frac{T}{5000}\right)^{0.417} (\mathrm{s}^{-1})$$
$$G_2(11,11) = 1.029\times 10^{-8} n_\mathrm{H}\left(\frac{T}{5000}\right)^{0.414} (\mathrm{s}^{-1})$$
$$G_4(11,11) = 0.0(\mathrm{s}^{-1})$$
$$G_0(22,22) = 7.6354\times 10^{-9} n_\mathrm{H}\left(\frac{T}{5000}\right)^{0.391} (\mathrm{s}^{-1})$$
$$G_2(22,22) = 1.046\times 10^{-8} n_\mathrm{H}\left(\frac{T}{5000}\right)^{0.399} (\mathrm{s}^{-1})$$
$$G_4(22,22) = 1.1088\times 10^{-8} n_\mathrm{H}\left(\frac{T}{5000}\right)^{0.421} (\mathrm{s}^{-1})$$
$$G_0(33,33) = 5.4956\times 10^{-9} n_\mathrm{H}\left(\frac{T}{5000}\right)^{0.379} (\mathrm{s}^{-1})$$
$$G_2(33,33) = 8.0887\times 10^{-9} n_\mathrm{H}\left(\frac{T}{5000}\right)^{0.383} (\mathrm{s}^{-1})$$
$$G_4(33,33) = 1.0839\times 10^{-8} n_\mathrm{H}\left(\frac{T}{5000}\right)^{0.396} (\mathrm{s}^{-1}) \tag{C.2}$$

$(J = 1/2, J = 3/2)$

$$Q_0(11,11) = 1.1761\times 10^{-9} n_\mathrm{H}\left(\frac{T}{5000}\right)^{0.4} (\mathrm{s}^{-1})$$
$$Q_2(11,11) = -4.1579\times 10^{-10} n_\mathrm{H}\left(\frac{T}{5000}\right)^{0.414} (\mathrm{s}^{-1})$$
$$Q_4(11,11) = 0.0(\mathrm{s}^{-1})$$
$$Q_0(22,22) = 2.5429\times 10^{-9} n_\mathrm{H}\left(\frac{T}{5000}\right)^{0.376} (\mathrm{s}^{-1})$$
$$Q_2(22,22) = -0.1636\times 10^{-9} n_\mathrm{H}\left(\frac{T}{5000}\right)^{0.302} (\mathrm{s}^{-1})$$
$$Q_4(22,22) = 0.2181\times 10^{-9} n_\mathrm{H}\left(\frac{T}{5000}\right)^{0.302} (\mathrm{s}^{-1}). \tag{C.3}$$

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