Ab initio calculation of the transfer and multipole rates of the Na ground state hyperfine levels perturbed by atomic hydrogen

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Abstract. A theoretical treatment of the multipole relaxation and transfer rates due to isotropic collisions is presented. Explicit expressions are obtained for the collisional rate constants of the hyperfine-structured ground level of the Na I atoms perturbed by collisions with H atoms. As the effects of Na nuclear spin during the collision are negligible, it is shown that all the rate constants involve the same electronic relaxation rate of the multipole of rank one. Evaluation of these rates has been carried out using very accurate potential energy curves. The formulae given here for the depolarizing collisional rates should be useful for accurately modeling the complex linear polarization pattern of the Na I doublet that can be observed in quiet regions of the solar atmosphere using spectro-polarimeters of high polarimetric sensitivity.

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

1. Introduction

Recent observations of linear polarization at the limb of the quiet Sun, performed with the high sensitivity polarimeter ZIMPOL (Stenflo & Keller 1997), have revealed a large number of unexpected phenomena and, in particular, have shown the existence of a complicated polarization pattern across the NaI doublet and of sharp polarization peaks in the cores of the D1 and D2 lines that are very difficult to explain without taking into account the atomic polarization of the hyperfine-structured ground level $3s^2 S_{1/2}$ of the Na I atom. This ground-level polarization is due to an optical depopulation pumping mechanism (Trujillo Bueno & Landi Degl'Innocenti 1997; Landi Degl'Innocenti, 1998; Trujillo Bueno 1999). As elastic collisions and non-vertical magnetic fields contribute to the depolarization of this lower state level, it is necessary to consider the scattering line polarization problem taking fully into account the atomic polarization of all the levels involved and the depolarization role of the collisions and magnetic fields.

The depolarization rates are usually estimated by an approximation based on the long-range C_6/R^6 van der Waals interac-

tion. As shown previously for broadening rates by collisions with hydrogen atoms (Faurobert-Scholl et al. 1995), the van der Waals approximation leads to a large underestimation of these rates.

The aim of the present paper is to give accurate results for all the collisional rates involving the hyperfine levels of the Na ground state. In Sect. 2, we show that, due to the small energy splitting of the hyperfine levels, all the relaxation rates of the hyperfine multiplet with electronic angular momentum $J = 1/2$ are proportional to the only non-zero electronic relaxation rate $g_1(J = 1/2)$ of rank 1, and we give their expression. In Sect. 3, we present detailed quantum mechanical calculations of the collisional cross sections and of the electronic relaxation rate g_1 using accurate potential energy curves. Finally, Sect. 4 gives some concluding remarks.

2. Multipole relaxation and tranfer rates: effects of nuclear spin

2.1. General theory

Under typical conditions of optical pumping, the internal states of the atoms are well described by a density matrix $\hat{\rho}$ which obeys a master (or rate) equation that governs its temporal evolution. As was first discussed by Fano (1963), the interaction of the atomic system with the perturbing gas is given by a relaxation matrix. Under the assumption that the impact approximation is valid, the relaxation matrix $\hat{G}$ is frequency independent and the corresponding term in the master equation is written:

$$\left(\frac{d\hat{\rho}}{dt}\right)_{rel} = -\hat{G}\hat{\rho} \tag{1}$$

In the impact approximation, valid at the low densities typical of stellar atmospheres, one assumes that the duration of a collision is much shorter than the free time between collisions so that binary collisions are dominant and the duration of the transient effects of collisions is negligibly short. Then, the relaxation matrix $\hat{G}$ can be expressed in terms of collisional amplitudes (Nienhuis 1976) or collision S or $T = 1 - S$ matrix elements (Fano 1963).

As the internal state distribution of the perturbers and the distribution of relative velocities are isotropic, the collisional relaxation of $\hat{\rho}$ is fully isotropic. Therefore, the relaxation matrix

$\hat{G}$ is considerably simplified by using an expansion in components T_q^k of irreducible tensorial sets (Fano 1949, 1954, 1957; Omont 1977; Blum 1981).

In a first step, we do not consider the hyperfine structure of the atoms. If we denote the internal states of the studied atoms as $\mid \lambda JM\rangle$, where J is the total angular momentum, M is the magnetic quantum number with respect to some arbitrary space fixed axis and λ indicates the possible other relevant quantum numbers, the matrix elements of the irreducible tensor T_q^k are defined by:

$$\langle \lambda JM \mid T_q^k(\lambda J, \lambda'J') \mid \lambda'J'M'\rangle =$$
$$\left(\frac{2k+1}{2J+1}\right)^{1/2} \langle JM \mid J'M'; kq\rangle \quad (2)$$

where $\langle JM \mid J'M'; kq\rangle$ is a Clebsch-Gordan coefficient.

If the different states $\mid \lambda J\rangle$ are well separated in energy, $\hat{\rho}$ is diagonal in λ and J and can be expressed as:

$$\hat{\rho} = \sum_{\lambda J}\sum_{kq} \rho_q^k(\lambda J)\, T_q^k(\lambda J, \lambda J)^\dagger \quad (3)$$

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

$$\left(\frac{d\rho_q^k(\lambda J)}{dt}\right)_{rel} = -\sum_{\lambda'J'} g_k(\lambda J, \lambda'J')\, \rho_q^k(\lambda'J') \quad (4)$$

A special case of interest for the Na ground state is the relaxation of the different multipoles of a Zeeman multiplet $\{\lambda J\}$ where the relaxation matrix is diagonal (Omont 1977).

$$\left(\frac{d\rho_q^k}{dt}\right)_{rel} = -g_k(\lambda J)\, \rho_q^k \quad (5)$$

In this equation g_k are the relaxation rates of the Zeeman multiplet ($g_0 = 0$). Expression of g_k in terms of the collisional S-matrix elements is given in paragraph 3.3.

The generalization of (5) to include the effects of the 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 $F =\mid J - I \mid, \mid J - I + 1 \mid, ..., J + I$ and we may consider possible off diagonal elements of the corresponding density matrix. The density matrix $\hat{\rho}$ can be expanded as:

$$\hat{\rho} = \sum_{FF'}\sum_{KQ} \rho_Q^K(FF')\, T_Q^K(FF')^\dagger \quad (6)$$

The density matrix for the electronic states can be expanded in terms of the tensors $T_{q_J}^{k_J}$ ($0 \leq k_J \leq 2J$) and similarly for the nuclear states, one can expand the density matrix on the $T_{q_I}^{k_I}$ tensor basis ($0 \leq k_I \leq 2I$). The unitary transformation from the basis $T_Q^K(FF')$ to the basis $T_{q_J}^{k_J} \otimes T_{q_I}^{k_I}$ is given by:

$$T_Q^K(FF') = \sum_{k_Jq_J}\sum_{k_Iq_I}[(2F+1)(2F'+1)]^{1/2}$$

$$[(2k_J+1)(2k_I+1)]^{1/2}$$
$$\begin{Bmatrix} J & I & F \\ J & I & F' \\ k_J & k_I & K \end{Bmatrix} \langle KQ \mid k_Jq_Jk_Iq_I\rangle T_{q_J}^{k_J}\, T_{q_I}^{k_I} \quad (7)$$

where $\{\ \}$ denotes a Wigner 9j-coefficient (Fano and Racah 1959).

It is well known that internal energy differences which correspond to frequency separations that are small compared to the inverse duration of a collision do not affect the scattering process. 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.

If the hyperfine Zeeman levels F of the multiplet are well defined, the time variation due to collisional relaxation of the element $\rho_Q^K(FF')$ is given by:

$$\left(\frac{d\rho_Q^K(FF')}{dt}\right)_{rel} = -\sum_{F''F'''} G_K(FF', F''F''')$$
$$\times \rho_Q^K(F''F''') \quad (8)$$

where the relaxation rates G_K are given by (Omont 1977):

$$G_K(FF', F''F''') = [(2F+1)(2F'+1)]^{1/2}$$
$$[(2F''+1)(2F'''+1)]^{1/2} \sum_{k_Jk_I}(2k_J+1)(2k_I+1)$$
$$\begin{Bmatrix} J & I & F \\ J & I & F' \\ k_J & k_I & K \end{Bmatrix} \begin{Bmatrix} J & I & F'' \\ J & I & F''' \\ k_J & k_I & K \end{Bmatrix} g_{k_J}(\lambda J) \quad (9)$$

2.2. Application to the Na ground state level

The ground state of the Na atom corresponds to an electronic angular momentum $L = 0$ and an electronic spin $S = 1/2$ so that the total electronic angular momentum is $J = 1/2$. The cross sections of collisions with H atoms between the ground state and the excited states of Na are very small and may be neglected. Therefore, we have only to consider the collisional relaxation of the $J = 1/2$ ground state, uncoupled with other states.

The nuclear spin of the Na atom is $I = 3/2$, which yields two hyperfine levels in the ground state, $F = 1$ and $F = 2$. The energy difference between those two levels is $\nu = 1771.6\,MHz$. The time duration τ of the Na+H collision can be estimated as follows: for a temperature of 5000 K, the relative velocity is $v \simeq 1.3\,10^6\,cm\,s^{-1}$. With an interaction range $R \simeq 8\,\text{Å}$ (see Fig. 1), $\tau \simeq 9.10^{-14}s$. Thus the frequency splitting is very small compared to the inverse of τ and the hyperfine splitting of the levels is negligible during the collision. We can apply Eq. (5) to obtain the relaxation rates of the Zeeman multiplet and then deduce from (9) all the relaxation rates between the hyperfine levels.

For $J = 1/2$, the only non-zero relaxation rate is $g_1(J = 1/2)$. The relaxation rates between the hyperfine levels, relevant for radiation polarization correspond to $K = 0, 1, 2$. $K = 0, 1$

contribute to circular polarization studies and $K = 0, 2$ to linear polarization. The non-zero rates are given by the following expressions in terms of g_1:

$K = 0$ $G_0(11,11) = 5/8 g_1$; $G_0(22,22) = 3/8 g_1$

$G_0(11,22) = G_0(22,11) = -\sqrt{15}/8 g_1$

$K = 1$ $G_1(11,11) = 11/16 g_1$; $G_1(22,22) = 7/16 g_1$

$G_1(11,22) = G_1(22,11) = -3\sqrt{5}/16 g_1$

$G_1(12,12) = G_1(21,21) = 15/16 g_1$

$G_1(12,21) = G_1(21,12) = 1/16 g_1$

$G_1(12,11) = G_1(11,12) = -\sqrt{5}/16 g_1$

$G_1(21,11) = G_1(11,21) = \sqrt{5}/16 g_1$

$G_1(21,22) = G_1(22,21) = 3/16 g_1$

$G_1(22,12) = G_1(12,22) = -3/16 g_1$

$K = 2$ $G_2(11,11) = 13/16 g_1$; $G_2(22,22) = 9/16 g_1$

$G_2(11,22) = G_2(22,11) = -\sqrt{21}/16 g_1$

$G_2(12,12) = G_2(21,21) = 13/16 g_1$

$G_2(12,21) = G_2(21,12) = 3/16 g_1$

$G_2(12,11) = G_2(11,12) = -3/16 g_1$

$G_2(21,11) = G_2(11,21) = 3/16 g_1$

$G_2(12,22) = G_2(22,12) = -\sqrt{21}/16 g_1$

$G_2(21,22) = G_2(22,21 = \sqrt{21}/16 g_1$.   (10)

## 3. Collision rates of the Zeeman multiplet $J = 1/2$

The results presented in the following paragraphs have been obtained from a quantum description of the collision using very accurate potential energy curves for NaH.

3.1. Interatomic potentials

The molecular states correlated to the Na(^2S)+ H(^2S) asymptote are the attractive $X^1\Sigma^+$ state and the repulsive $a^3\Sigma^+$ state. The Gaussian basis sets employed for their calculation are general contractions based on atomic natural orbitals. The basis sets include for hydrogen and sodium the primitive basis set $[6s, 4p]$ and $[13s, 10p, 4d]$ of Sadlej(1991) contracted to $[3s, 2p]$ and $[7s, 5p, 2d]$ respectively. The total number of contracted Gaussian functions was 41.

To obtain the best accuracy for the potential energy, multireference configuration interaction (MRCI) wave functions were constructed using multiconfiguration self-consistent field (MC-SCF) active space (Werner & Knowles 1985, 1988, Knowles & Werner 1985, 1988) with core and valence orbitals ($1\sigma - 7\sigma, 1\pi - 2\pi$). The MRCI wave functions accounted for more than 4 millions of configurations which were internally contracted to 250 thousands. All the calculations have been performed with the MOLPRO code[1]. Our results compare well
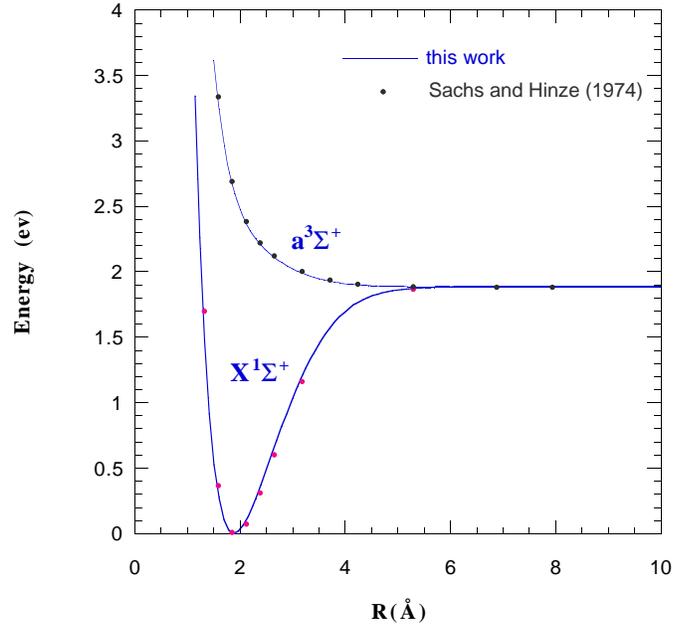
Fig. 1. Potential curves from the present calculations (solid line) and from Sachs & Hinze (1974) (dotted line)

Table 1. Calculated and experimental spectroscopic constants for the $X^1\Sigma^+$ state of $^{23}Na^1H$

Reference	R_e (a_0)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})
this work	3.567	1169	22.8
Huber & Herzberg 1979	3.567	1172	19.7
Sachs & Hinze (1974)	3.609	-	-

with previous results of Sachs & Hinze (1974) at the scale of the figure (Fig. 1).

In order to test the basis set and the active space, the minimum R_e of the attractive $X^1\Sigma^+$ state was determined. A fit of the first vibrational levels yielded the harmonic frequency ω_e and the anharmonicity constant $\omega_e x_e$. The vibrational levels were obtained from numerical integration of the radial Schrödinger equation using the Numerov method (Johnson 1977). The calculated values of these spectroscopic constants are given in Table 1 for comparison with the experimental results (Huber & Herzberg 1979) and the theoretical results obtained by Sachs & Hinze (1974). Our results agree very well with the experiment and improve the previous theoretical results.

3.2. Dynamics of the collision

The quantum mechanical formulation of the collision is that given by Mies (1973) and generalized by Launay and Roueff (1977). A sodium 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 $J^T = j + l$ and its space fixed projection M^T are conserved during the collision. It is convenient to use scattering channel states $| Jj_2jlJ^T \rangle$ which describe the asymptotic fragments with relative angular momentum l. The total wave function is expanded in terms of these channel states, the expansion coefficients are the radial amplitudes $F^{J^T}_{J'j_2j'l', Jj_2jl}$ which satisfy the usual coupled radial equations (Spielfiedel et al. 1991). These radial equations which describe the relative motion of the two atoms depend on the electrostatic interaction potential at each internuclear distance R. The asymptotic form of the radial equations define the T-matrix elements (Spielfiedel et al. 1991).

In the particular case of the Na atom in its ground state ($J = 1/2$) colliding with an H atom in its ground state ($j_2 = 1/2$), the channels for a given angular momentum J^T are the following: $| 1 \rangle = | \frac{1}{2}\frac{1}{2}0J^TJ^T \rangle$; $| 2 \rangle = | \frac{1}{2}\frac{1}{2}1J^TJ^T \rangle$; $| 3 \rangle = | \frac{1}{2}\frac{1}{2}1J^T - 1 J^T \rangle$; $| 4 \rangle = | \frac{1}{2}\frac{1}{2}1J^T + 1 J^T \rangle$.

From the general equations (Spielfiedel et al. 1991), it can be shown that these channels are uncoupled and that the radial amplitudes $F^{J^T}_{J'j_2j'l', Jj_2jl}(R)$ are just given by:

$$\left(\frac{d^2}{dR^2} - \frac{l(l+1)}{R^2} + k_j^2 \right) F^{J^T}_{J'j_2j'l', Jj_2jl}(R) =$$
$$2\mu V_{\Lambda S}(R) F^{J^T}_{J'j_2j'l', Jj_2jl}(R) \tag{11}$$

μ is the reduced mass of the colliding system, k_j is the wave number defined by $k_j^2 = 2\mu E$ where E is the kinetic energy. $V_{\Lambda S}(R)$ is the adiabatic interatomic potential corresponding to $V_{X^1\Sigma^+}$ for channel 1 and $V_{a^3\Sigma^+}$ for channels 2, 3, 4. The asymptotic form of the radial function F is just proportional to $sin(k_jR - l\frac{\pi}{2} + \delta_l)$ where δ_l is the phase shift. From δ_l we obtain the S-matrix element $S_l = exp(2i\delta_l)$ and the T-matrix element $T_l = 1 - S_l$.

3.3. Relaxation constant $g_k(J)$ of the electronic ground state

As inelastic cross sections are negligible, it can be shown (Spielfiedel et al. 2000), that the relaxation constants g_k of the electronic ground state J is given by:
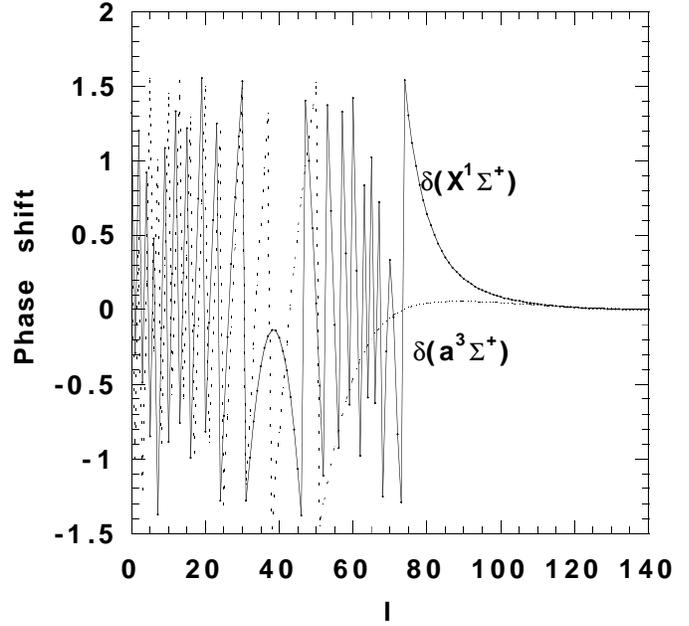
$$g_k(J) = n_H \int_0^\infty vf(v)dv\Lambda_k(J) \tag{12}$$

where n_H is the perturber (H atom) density, v is the relative velocity and the cross section $\Lambda_k(J)$ has the following expression:

$$\Lambda_k(J) = \sum_m \frac{2m+1}{2J+1}[1 - (-1)^{2J+k+m}(2J+1)$$
$$\left\{ \begin{matrix} m & J & J \\ k & J & J \end{matrix} \right\}]B(JJ;m) \tag{13}$$

with:

$$B(JJ;m) = \frac{\pi}{(2j_2+1)k_j^2} \sum_{j_bj_b'll'} (2j_b+1)(2j_b'+1)$$

Fig. 2. Variation of the phase shift δ_l versus l for the $X^1\Sigma^+$ and $a^3\Sigma^+$ potentials: $E = 0.5$ eV (full line: $\delta_l(X^1\Sigma^+)$; dotted line: $\delta_l(a^3\Sigma^+)$).

$$| \sum_{J^Tjj'} \sqrt{(2j+1)(2j'+1)}(2J^T+1)$$
$$(-1)^{J+j_2+J^T} \left\{ \begin{matrix} J & j_2 & j \\ l & J^T & j_b \end{matrix} \right\} \left\{ \begin{matrix} J & j_2 & j' \\ l' & J^T & j_b' \end{matrix} \right\} \left\{ \begin{matrix} J & J & m \\ j_b & j_b' & J^T \end{matrix} \right\}$$
$$\langle Jj_2j'l'J^T \mid T \mid Jj_2jlJ^T \rangle |^2 \tag{14}$$

In the particular case studied here, $j = j'$ and $l = l'$ (uncoupled T-matrix elements). The $B(JJ;m)$ coefficients generalize the Grawert factors of Reid (1973) defined for a perturber with $j_2 = 0$ angular momentum. In the case under study, $k = 1$ and $m = 1$ and $\Lambda_1 = 2B\left(\frac{1}{2}\frac{1}{2}, 1\right)$.

3.4. Results

The typical variations of the phase shifts $\delta_l(X^1\Sigma^+)$ and $\delta_l(a^3\Sigma^+)$ with l (Fig. 2) exhibit rapid oscillations for the lower values of l. Such behaviour is usual and may be explained by successive increments of π of the phase shift (Child 1974). One also notices a stationary phase point around $l = 40$ of the $\delta_l(X^1\Sigma^+)$ phase shifts characteristic of phase shifts in attractive potentials.

Fig. 3 shows the energy dependence of the cross section $\Lambda_1(J = 1/2)$. An important feature is the appearance of oscillations in the low energy range. These oscillations are due to resonances in the attractive part of the molecular $X^1\Sigma^+$ potential. These oscillations disappear after averaging over the velocities (see Fig. 4). The variation of the rate coefficient $g_1(J = 1/2)$ with the temperature is very smooth and can be fitted by the following expression:

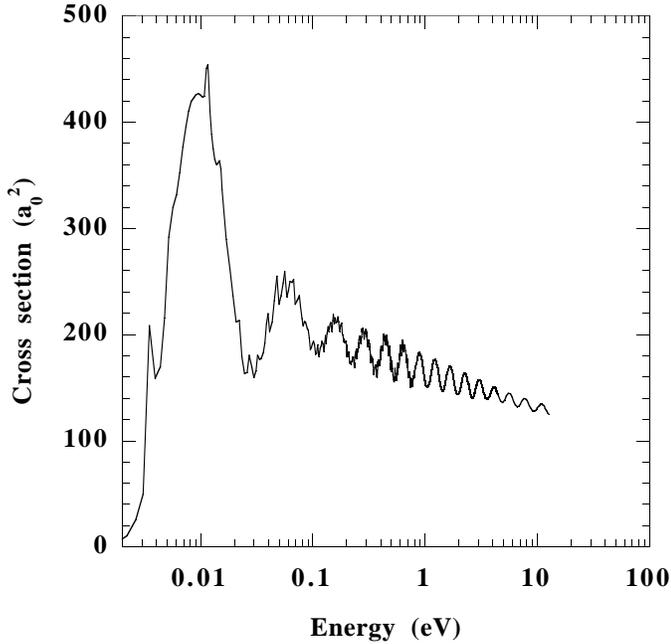$$g_1 = 3.65 \, 10^{-10} n_H(T/5000)^{1.42} \, (s^{-1}) \tag{15}$$

Fig. 3. Depolarization cross section Λ_1 as function of energy

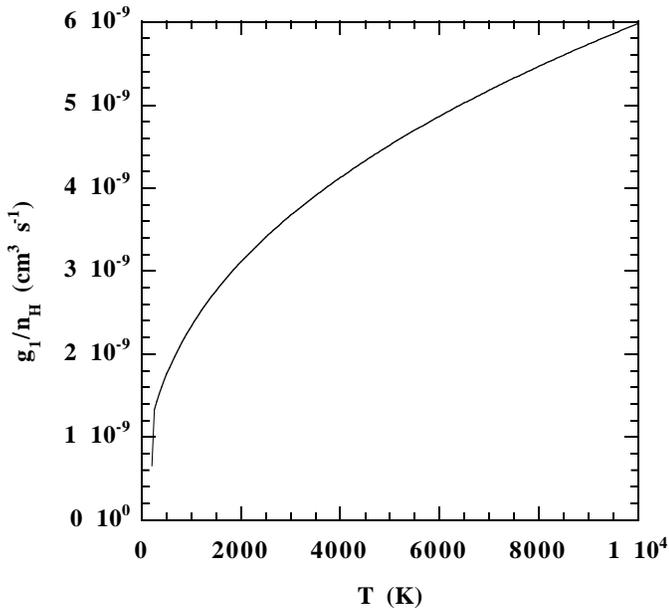**Fig. 4.** Relaxation rate $g_1/n_H (cm^3 s^{-1})$ as function of temperature $T(K)$.

4. Concluding remarks

As mentioned in the introduction, the problem is to determine whether the collisions with H atoms depolarize or not the ground state of the Na atoms. As the linear polarization of the ground state is due to an optical pumping process by the radiation field, the collisional rates G_2 have to be compared to BJ where B is the Einstein coefficient in absorption and J is the mean intensity of the radiation field (Landi Degl'Innocenti 1999). Assuming that $BJ = 10^{-3}A$ where $A \simeq 10^8 s^{-1}$ is the spontaneous emission rate, the collisional depolarization occurs if $G_2 \geq 10^5 s^{-1}$. As the G_2 coefficients are of the order of magnitude as g_1 and assuming a temperature of 5000 K, we can conclude that the hydrogen density n_H cannot be larger than a fraction of $10^{15} cm^{-3}$ in the region of formation of the D_1 and D_2 lines.

Of course, this upper limit of n_H is just a crude estimate, and the correct diagnostic requires the resolution of the non LTE multi-level rate equations that govern the temporal evolution of the atomic density matrix (Trujillo Bueno & Landi Degl'Innocenti 1997). This implies that all the inelastic collision cross sections that contribute to the population of the Na level are known. This work is in progress.

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