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Depolarizing isotropic collisions of the CN solar molecule with electrons

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Abstract Existence of linear polarization, formed by anisotropic scattering in the photosphere, has been demonstrated observationally as well as theoretically and is called second solar spectrum (SSS). The SSS is distinguished by its structure, which is rich in terms of information. In order to analyze the SSS, it is necessary to evaluate the (de)polarizing effect of isotropic collisions between CN solar molecules and electrons or neutral hydrogen atoms. This work is dedicated to calculations of the polarization transfer rates associated with CN–electron isotropic collisions. We show that usual rates serve as a proxy for polarization transfer rates. Then, we take advantage of available usual excitation collisional rates obtained via sophisticated quantum methods in order to derive the polarization transfer rates for the $X \, {}^{2}\Sigma^{+} - B \, {}^{2}\Sigma^{+}$ (violet) and $X \, {}^{2}\Sigma^{+} - A \, {}^{2}\Pi$ (red) systems of CN. Our approach is based on the infinite order sudden (IOS) approximation and can be applied for other solar molecules. We discuss the effectiveness of collisions with electrons on the SSS of the CN lines. Our results contribute to reducing the degree of complication in modeling the formation of the SSS of CN.

Key words: collisions - Sun: photosphere - molecular processes - light polarization

1 INTRODUCTION

Diatomic molecules, like CN, present in cool regions of the solar photosphere have a remarkably conspicuous and rich second solar spectrum (SSS) because of their multiple electronic, vibrational and rotational states. Complexity of molecular spectra gives rise to many polarized lines contained in a narrow spectral window and, thus, can be observed simultaneously. Simultaneous spectropolarimetric observations provide an exceptional opportunity to extract quiet Sun magnetic fields by applying the differential Hanle effect tool (e.g., Hanle 1924; Faurobert & Arnaud 2003; Berdyugina & Fluri 2004; Asensio Ramos & Trujillo Bueno 2005; Derouich et al. 2006). It can be noticed that the (de)polarizing effect of collisions and the Hanle effect are mixed in the same observable which is the SSS - this makes the SSS interpretation difficult. Independent determination of the collisional effects permit minimizing the number of unknowns in the interpretation of the SSS formation.

Under the influence of isotropic collisions between CN molecules and hydrogen atoms or electrons, states are excited and lines can be strongly affected. Qutub et al. (2020) investigated the (de)polarizing effect of CN collisions with hydrogen atoms. The aim of our present work is to complement the Qutub et al. study by treating the (de)polarizing effect of {CN-electron} collisions.

Several studies are concerned with usual excitation collisional rates like the excitation, shift and broadening rates of spectral lines (e.g., Roueff & Lique 2013). These usual rates correspond to the particular case where only Stokes-I is studied. First, cross-section calculations for the electron-impact rotational excitation of CN states were based on the Born approximation (Thaddeus & Clauser 1996). Then, more accurate close-coupling calculations were performed by Allison & Dalgarno (1971) and Thaddeus (1972). More recently, Harrison & Tennyson (2012) revisited the excitation of the CN radical by collisions with electrons applying a sophisticated Rmatrix quantum approach combined with the infinite order sudden (IOS) approximation to derive electronimpact spin-coupled cross-sections. It is of great practical importance to use these accurate quantum cross-sections as a proxy for polarization transfer rates.

If one is interested in the polarization state (i.e., Stokes-Q, U and V), collisional depolarization and polarization transfer rates must be studied and determined (i.e.,

Derouich et al. 2003; Qutub et al. 2020; Derouich 2020). In this paper, we provide a method allowing calculation of polarization transfer rates through the available data¹ of usual rates published by Harrison & Tennyson (2012). This is possible thanks to implementation of the IOS approximation which is particularly valid due to the high solar temperatures (e.g., Pack 1972, 1974). Once polarization transfer rates are obtained, solar application is discussed.

2 POLARIZATION TRANSFER DUE TO INELASTIC COLLISIONS

Theoretically, isotropic collisions with electrons can play a depolarizing role inside the same electronic level of the molecule. However, energy spacings between consecutive molecular rotational levels within the same electronic level are given by $\Delta E_R = BN(N+1) - BN(N-1)$ 1) = 2BN where B is the rotational constant of the CN molecule and N is the rotational number; B = $1.9 \text{ cm}^{-1} = 2.36 \times 10^{-4} \text{ eV}$ (Harrison & Tennyson 2012) and one can consider a typical value of N = 5. So, ΔE_R is of the order of 2 meV (1 meV = 10⁻³ eV) (see also Itikawaa & Masonb 2005). ΔE_R clearly corresponds to electrons' small relative velocity of $\sim 26 \,\mathrm{km}\,\mathrm{s}^{-1}$. Thus, rotational transitions play a significant role only for collisions involving slow velocity of electrons in extremely low temperature media (see Itikawaa & Masonb 2005). In the case of the solar atmosphere, electrons have larger velocities able to excite the molecule from one electronic level to another rather than a purely rotational excitation. In the solar context, it is commonly accepted that, for the case of collisions with electrons, only collisional transitions between two different electronic levels are of interest.

Let us consider that CN molecular polarized lines, associated with $X \ ^{2}\Sigma^{+}-B \ ^{2}\Sigma^{+}$ and $X \ ^{2}\Sigma^{+}-A \ ^{2}\Pi$ transitions, undergo the effect of isotropic collisions with electrons. $X \ ^{2}\Sigma^{+}$, $B \ ^{2}\Sigma^{+}$ and $A \ ^{2}\Pi$ states are supposed to be polarized in the sense that their Zeeman sub-levels are unequally populated and quantum interferences exist among them (e.g., Derouich et al. 2003; Derouich 2020). The signature of such a polarization can be observed in the SSS. In the photosphere where the SSS forms, collisions with electrons are mainly isotropic. Under the influence of isotropic collisions, theoretically, the polarization can be partially or completely destroyed. A collisional (de)polarization matrix should be expanded on a suitable irreducible tensorial operator (ITO) basis T_{q}^{k} (e.g., Sahal-Bréchot 1977; Trujillo Bueno 2001; Derouich et al. 2003; Landi Degl'Innocenti & Landolfi 2004; Derouich 2020). In the ITO basis, k is the tensorial order and q is associated with interferences between the Zeeman-sublevels within the polarized atomic state (e.g., Landi Degl'Innocenti & Landolfi 2004). Quantification of the molecular states is efficiently achieved by employing density matrix elements ρ_q^k expanded over the ITO basis (e.g., Sahal-Bréchot 1977; Landi Degl'Innocenti & Landolfi 2004).

Since collisions are isotropic, all polarization transfer rates are q-independent (e.g. Sahal-Bréchot 1977; Derouich et al. 2003). Thus one needs only to calculate the values of polarization transfer rates for one q-value (e.g., q = 0) and use these values for quantifying the effect of collisions on all ρ_q^k terms independently of their q-values.

By adopting the coupling schemes illustrated, for example, by Harrison et al. (2012) and Corey & Smith (1985) one has

$$\begin{split} \sigma_{\rm IOS}^k(e_i \; Nj \to e_f \; N'j', E) &= \\ \sum_{K_j} (-1)^{k+j'+K_j+j+1} (2j+1)(2j'+1)(2N+1)(2N'+1) \\ \left\{ \begin{array}{cc} N & N' \; K_j \\ j' \; \; j \; \; S_m \end{array} \right\}^2 \times \left\{ \begin{array}{cc} j \; \; j' \; K_j \\ j' \; \; j \; \; K_m \end{array} \right\} \end{split} \tag{1} \\ \left(\begin{array}{cc} N' \; N \; K \\ 0 \; \; 0 \; 0 \end{array} \right)^2 \sigma_{\rm IOS}(e_i 0 \to e_f K, E) \,, \end{split}$$

where $\sigma_{IOS}^k(e_i \ Nj \rightarrow e_f \ N'j', E)$ is the polarization transfer cross section within the framework of the IOS approximation (i.e., Derouich et al. 2020). *E* is the relative kinetic energy, *N* is the rotational number of the CN, S_m is the CN spin number, $j = S_m + N$, e_i is the electronic CN lower state and e_f is the electronic upper state. In the present work, e_i represents $X \ ^2\Sigma^+$ or $B \ ^2\Sigma^+$ states and e_f represents $A \ ^2\Pi$ state.

The K_j number quantifies the angular momentum carried between the states during the collision. The possible values of K_j are given by the triangle inequalities contained in the six *j*-symbols of Equation (1). The 3j-coefficients $\binom{N' \ N \ K_j}{0 \ 0 \ 0}$ are identically zero unless the sum $N + N' + K_j$ is even. Since the energy separations between the vibrational/rotational levels of the same electronic state are **much** smaller than the separation between the electronic states, we assume that σ_{IOS} is associated with the excitation among electronic states without taking into account vibrational or rotational numbers. It means that $\sigma_{\text{IOS}}(e_i 0 \to e_f K) \simeq \sigma(e_i \to e_f)$.

Harrison & Tennyson (2012) obtained electron-impact excitation cross-sections $\sigma(e_i \rightarrow e_f)$ from the ground state $X \ ^2\Sigma^+$ to the CN excited states $B \ ^2\Sigma^+$ and $A \ ^2\Pi$. Crosssections of Harrison & Tennyson (2012) are determined for electron impact energies up to 10 eV, for different quantum scattering models. These energies allow us to obtain the

¹ Collision data have been extracted from graphics presented in Harrison & Tennyson (2012) by utilizing the "xyExtract" software. We verified that the precision of the data extraction does not practically influence calculation of the polarization transfer rates.

polarization transfer rates $C^k(e_i \ Nj \rightarrow e_f \ N'j', T)$ for photospheric solar temperatures.

Rates $C^k(e_i \ Nj \rightarrow e_f \ N'j',T)$ are obtained through an integration over Maxwellian velocity distribution of $[n_e \times v \times \sigma_{IOS}^k(e_i \ Nj \rightarrow e_f \ N'j')]$, where $\sigma_{IOS}^k(e_i \ Nj \rightarrow e_f \ N'j')$ is the polarization transfer cross section, v is the relative velocity and n_e is the electron density (see e.g., Flower 1990).

The IOS approximation is suitable in our work for two reasons:

- It has an acceptable precision since the collision energy is large for solar temperatures (e.g., Derouich et al. 2020). In addition, it is implemented in the scattering calculations of $\sigma(e_i \rightarrow e_f)$ by Harrison & Tennyson (2012).
- Only in the framework of the IOS approximation is it possible to express the $C^k(e_f \ N'j' \rightarrow e_i \ Nj)$ as a linear combination of the standard collisional rates (see Eq. (1)).

The IOS approximation became very useful since it was proposed more than 40 years ago (e.g., Pack 1972, 1974; Goldflam et al. 1977; Corey & Alexander 1985; Corey et al. 1986; Derouich 2006; Lique et al. 2006). Generally speaking, the IOS approximation can be well-adopted in the solar context. We notice that the efficiency and accuracy of the IOS approximation during collisions of the CN molecule in the $^{2S+1}\Sigma^+$ states with electrons were discussed by Harrison et al. (2012). They showed that, for the range of energies considered in this work, there is excellent agreement between full close coupling calculations and those based on IOS approximation.

Variation rate of $\rho_q^k(e_i \quad Nj)$ in the statistical equilibrium equations (SEE) is given in Derouich et al. (2020). It is of great importance to correctly evaluate the collisional contribution in order to clarify whether it has an effect on the CN scattering polarization or not. This would remove an ambiguity which may arise in the SSS modeling.

3 POLARIZATION TRANSFER RATE CALCULATIONS

We utilized the Harrison & Tennyson (2012) theoretical scattering cross-sections as a proxy to obtain the polarization transfer rates because they are the most accurate available cross-sections. According to Harrison & Tennyson (2012), theoretical threshold² energies are $\Delta E = 1.515$ eV for the $A^{-2}\Pi$ excited state and $\Delta E = 3.491$ eV for the $B^{-2}\Sigma^{+}$ state. On the other hand, experimental values of Huber & Herzberg (1997) are $\Delta E = 1.151$ eV and $\Delta E = 3.197$ eV for the $A^{-2}\Pi$ and $B^{-2}\Sigma^+$, respectively. So, error bars on the ΔE calculations are 32% for the A $^{2}\Pi$ excited state and 9% for the $B^{-2}\Sigma^+$ state. Let us mention that typically when ΔE increases, collisional rate decreases. Thus, error bars on ΔE calculations will result in inaccuracies of the collisional rate calculations. In addition, Harrison & Tennyson (2012)'s binding energy of the ground state $X^{2}\Sigma^{+}$ is 3.407 eV but the experiment gives 3.86 eV; it means that the error percentage in determining the binding energy is 11%. Harrison & Tennyson (2012)'s dipole moment agrees within 10% against the experimental values of Thompson & Dalby (1968). Because these error percentages are not remarkably large, our conclusions will not be affected by errors in the Harrison & Tennyson (2012) results. Furthermore, in the absence of better results, one must exploit Harrison & Tennyson (2012) to obtain a reasonable estimation of the collisional effects on the polarization since such effects are completely unknown.

Harrison & Tennyson (2012) used the so-called Quantemol-N software combined with sophisticated Rmatrix codes. Although the R-matrix procedure can produce the standard Hartree-Fock (HF) orbitals, Harrison & Tennyson (2012) employed the well known MOLPRO package to produce natural orbitals (NOs) by utilizing multi-reference configuration interaction (MRCI). The use of NOs greatly improves the scattering cross-section results as can be verified by examining figure 2 of Harrison & Tennyson (2012) who mentioned that their NO-based calculations must be regarded as their best estimate for the scattering cross-sections. We applied these cross-sections in our present work.

Results of Harrison & Tennyson (2012) were obtained for a range of kinetic energies ranging from 0 to 10 eV which permits determining collision rates for temperatures up to 10000 K. Figure 1 features an example of computations of polarization transfer between molecular level with j' = 5.5 which belongs to the upper electronic state and j = 4.5 (lower electronic state). To explore whether or not collisions are important, one must obtain a value representative of the highest polarization rates. If these large values do not influence the degree of polarization, then smaller values will not be able to influence such polarization. It is for this reason that we have chosen small values of $\Delta j = |j' - j| = 1$ where the maximum values of the polarization transfer rates are reached. Our conclusions in this work will not be affected by this choice of the values j and j'.

Figure 1 depicts polarization transfer rates from the state $X^{-2}\Sigma$ to $B^{-2}\Sigma$, and from $X^{-2}\Sigma$ to $A^{-2}\Pi$. It is

 $^{^2\,}$ The threshold energy is the energy needed to excite the electron from the ground state to the excited state.

these transitions which are of interest in solar magnetism diagnostics. Calculation of every rate is performed for a fixed medium temperature T. By sufficiently repeating the calculations, rates are obtained for temperatures ranging from 1500 K to 10 000 K. All rates are computed for k = 0, k = 1 and k = 2. We made the choice to collect them in a more compact form as variation laws characterized by the tabulated values of a^k (in cm³ s⁻¹) and b^k (in cm³ s⁻¹):

$$C^{k}(e_{i} N j \to e_{f} N' j') = n_{e} \left[a^{0} + a^{1}\left(\frac{T}{5000}\right) + a^{2}\left(\frac{T}{5000}\right)^{2}\right],$$
(2)

$$C^{k}(e_{i} N j \to e_{f} N' j') = n_{e} \left[b^{0} + b^{1} \left(\frac{T}{5000}\right) + b^{2} \left(\frac{T}{5000}\right)^{2} + b^{3} \left(\frac{T}{5000}\right)^{3} + b^{4} \left(\frac{T}{5000}\right)^{4}\right],$$

where the coefficients a^k and b^k are provided in Table 1 and n_e is considered in cm⁻³. We notice that, since the SSS is exclusively related to even tensorial orders k (see e.g., Derouich et al. 2003), only rates with orders k = 0, k = 1 and k = 2 are given. The analytical relationships of Equation (2), giving the rates as functions of the temperatures, are obtained with a correlation coefficient R>0.99. These relationships are useful for solar applications and can be easily included in the radiative transfer numerical codes.

From the principle of detailed balance, collisional rates $C^k(e_f \ N'j' \rightarrow e_i \ Nj)$ can be derived from the following relation

$$C^{k}(e_{f} N'j' \rightarrow e_{i} Nj, T) = \frac{2j+1}{2j'+1} \exp\left(\frac{E_{j'} - E_{j}}{k_{B}T}\right)$$
$$C^{k}(e_{i} Nj \rightarrow e_{f} N'j', T),$$
(3)

where k_B is the Boltzmann constant and E_j is the energy of the level (j).

By applying the variation laws expressed in Equation (2) at T = 6500 K, we find that for the transition

-
$$X^{2}\Sigma \rightarrow A^{2}\Pi$$
 where $j = 4.5$ and $j' = 5.5$:

$$C^{0}(e_{i} \ Nj \to e_{f} \ N'j', T) = n_{e} \times 19.241 \times 10^{-10} \ (\text{s}^{-1}),$$

$$C^{1}(e_{i} \ Nj \to e_{f} \ N'j', T) = n_{e} \times 14.665 \times 10^{-10} \ (\text{s}^{-1}),$$
(4)

$$C^{2}(e_{i} \ Nj \to e_{f} \ N'j', T) = n_{e} \times 11.099 \times 10^{-10} \ (\text{s}^{-1}).$$

and for the transition:

– for the state $X~^2\Sigma \rightarrow B~^2\Sigma$ with j=4.5 and j'=5.5:

$$\begin{split} C^{0}(e_{i} \; Nj \rightarrow e_{f} \; N'j', T) &= n_{e} \times 0.157 \times 10^{-10} \; (\mathrm{s}^{-1}), \\ C^{1}(e_{i} \; Nj \rightarrow e_{f} \; N'j', T) &= n_{e} \times 0.121 \; 10^{-10} \times (\mathrm{s}^{-1}), \; (5) \\ C^{2}(e_{i} \; Nj \rightarrow e_{f} \; N'j', T) &= n_{e} \times 0.093 \times 10^{-10} \; (\mathrm{s}^{-1}), \end{split}$$

where the density n_e is given in cm³.

It is clear that rates associated with the $X^{-2}\Sigma \rightarrow A^{-2}\Pi$ transition are clearly larger than polarization transfer rates between $X^{-2}\Sigma$ and $B^{-2}\Sigma$ states. In the next section, we consider values of these rates to explore the effect of collisions with electrons on the SSS.

4 ARE COLLISIONS WITH ELECTRONS ABLE TO AFFECT THE SSS OF CN?

For very first explorations, one has to compare the polarization transfer rates to the Einstein coefficients $A_{e_i e_f}$ of the studied line transition in order to decide on the possibility of collisional effect on the SSS of CN.

As can be found, for example in Berdyugina (2009) (see also Qutub et al. 2020), for some selected lines of the $B^2\Sigma - X^2\Sigma$ system in the bandhead (3839.136 Å - 3883.114 Å), Einstein coefficients for spontaneous emission A_{BX} are $\simeq 7 \times 10^6$ s⁻¹. For effective photospheric temperature $T_{\rm eff} = 5780$ K and for typical values of photospheric electron density $n_e = 10^{12} \text{ cm}^{-3}$, by utilizing Equations (2) and (3), we calculate the largest de-excitation rate $C^0(e_f \ N'j' \rightarrow e_i \ Nj,T)$ $\sim n_e 47 \times 10^{-12} \text{ s}^{-1} \sim 47 \text{ s}^{-1}$. For $n_e = 10^{12} \text{ cm}^{-3}$, $C^0(e_f N'j' \rightarrow e_i Nj, T) << A_{BX}$ which means that lines associated with the $B^2\Sigma - X^2\Sigma$ are completely immune to isotropic collisions with electrons. One can conclude that inelastic collisions with electrons can be safely neglected for modeling lines of SSS for the $B^2\Sigma$ – $X^2\Sigma$ system.

On the other hand, according to Brooke et al. (2014), the Einstein coefficient associated with transitions within the X $^{2}\Sigma - A$ $^{2}\Pi$ system is $A_{AX} = 6.5 \times 10^{4} \text{ s}^{-1}$ for cases where initial and final vibrational levels are v = 0. In addition, by applying Equations (2) and (3) for $X^{2}\Sigma \to A^{2}\Pi$, de-excitation rates $C^{0}(e_{f} N'j' \to$ $e_i \ Nj,T) \sim n_e \ 1132.5 \times 10^{-9} \ s^{-1} \sim 1.13 \times 10^6 \ s^{-1}$ for $n_e = 10^{12} \ cm^{-3}$. Hence, $\frac{C^0(e_f \ N'j' \rightarrow e_i \ Nj,T)}{A_A \ x} \sim 17$ which means that collisional effects are high enough to completely depolarize the $A^{-2}\Pi$ state. In addition, for transitions occurring in the vibrational band (v = 0 - v =2), $A_{A X} \sim 2 \times 10^3$ (see Brooke et al. 2014) which is much smaller than $C^0(e_f \ N'j' \to e_i \ Nj, T)$ and in this case also the state is depolarized by isotropic collisions. Let us notice that values of the Einstein coefficient A_{AX} depend on the j and v-values, but also on the so-called Λ -doubling (Brooke et al. 2014 and also, e.g., Whiting & Nicholls 1974; Whiting et al. 1980) which must be taken into account in accurate calculations of the SSS.

5 CONCLUDING REMARKS

Polarized states of CN molecules undergo the effect of collisions with most abundant perturbers in the



Fig. 1 Rates C^k due to isotropic collisions with electrons for 1000 K $\leq T \leq 10000$ K.

Table 1 Case of the transition: $X \ ^{2}\Sigma \rightarrow A \ ^{2}\Pi$: coefficients a^{0} , a^{1} and a^{2} in $[10^{-10} \text{ cm}^{3} \text{ s}^{-1}]$. Case of the transition: $X \ ^{2}\Sigma \rightarrow B \ ^{2}\Sigma$: coefficients b^{0} , b^{1} , b^{2} , b^{3} and b^{4} in $[10^{-10} \text{ cm}^{3} \text{ s}^{-1}]$.

k	a^0	a^1	a^2	b^0	b^1	b^2	b^3	b^4
0	2.026	-15.	21.725	$-8.5 imes 10^{-2}$	0.411	-0.235	-0.614	0.509
1	1.560	-11.662	16.725	-6.548×10^{-2}	0.317	-0.181	-0.473	0.392
2	1.183	-8.860	12.683	-4.963×10^{-2}	0.240	-0.137	-0.358	0.297

solar photosphere, namely neutral hydrogen atoms and electrons. In order to cleanly interpret the polarization of CN lines in terms of solar magnetic fields, the (de)polarizing collisional effect has to be evaluated without ambiguity. Regardless of whether collisions with electrons are efficient or not, quantitative knowledge of their effect permits minimizing the number of unknowns in modeling the SSS formation.

The effect of collisions with electrons on the solar molecular polarization is not well known. Let us mention that electrons present in the photosphere result essentially from ionization of metals. If the rates of collisions with electrons are unknown, results inferred from the interpretation of the SSS can be blurred. These rates are an essential ingredient—often overlooked—for a proper understanding of the polarized solar spectrum. As an example, a rate of depolarization can be wrongly attributed to collisions with electrons although it can be most likely due to the Hanle effect of magnetic fields.

It can to be noticed that, especially for solar molecules, rates of different types of collisions are not well known. Recently, a first study concentrated on collisions between neutral hydrogen and the CN molecule in its ground state $X^{2}\Sigma^{+}$ (Qutub et al. 2020). Density of the photospheric electrons is generally about three or four orders of magnitude lower than the hydrogen atom density.

We obtained quantum polarization transfer rates for the CN violet and red systems, $X^{2}\Sigma^{+}-B^{2}\Sigma^{+}$ and $X^{2}\Sigma^{+}-A^{2}\Pi$, respectively. The main conclusion of this work is that collisions with electrons can be safely neglected for the case of the $X^{2}\Sigma^{+}-B^{2}\Sigma^{+}$ violet system due to the small values of the collisional coefficients for tensorial orders k = 0, 1 and 2. On the contrary, great caution must be exercised if one models the polarization of the $X^{2}\Sigma^{+}-A^{2}\Pi$ red system due to large values of polarization transfer rates when compared to Einstein coefficients.

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