PROBING Na–Na* RESONANT COLLISIONS MECHANISMS WITH STRONG MAGNETIC FIELDS

J.C. GAY and W.B. SCHNEIDER*

*Laboratoire de Spectroscopie Hertzienne * de l'Ecole Normale Supérieure 4, Place Jussieu 75230 Paris Cedex 05, France*

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We report the experimental study of excitation transfer in strong magnetic fields between the $m = -3/2$ and $m = 3/2$ Zeeman sublevels of the $3^2P_{3/2}$ state of Na, in Na–Na* resonant collisions. A huge decrease of the transfer rate between 6 and 70 kG is observed and shown in good agreement with theoretical predictions obtained with a cut-off method. Some insights on the mechanisms of the process are deduced and the particularly important role of the electronic spin of the ground state p· rturbers is emphasized.

Strong magnetic fields are of particular interest for studying weakly inelastic collisions in a vapour [1–4]. Indeed they offer a very simple method for continuously varying the energy difference between the Zeeman substates of an atom over a considerable energy range of about $kT/10$ currently obtained with steady fields. This provides with large possibilities of reliable comparison between experiments and theory [3, 5]. The magnetic field effect on the collisional process in a vapour is a twofold one. The parameters describing the relaxation are field dependent.[5]. The lack of invariance of the field under time reversal and spatial rotations produces a break down of the rotational invariance [5–7] generally verified in zero field. These effects are important when the energy difference between the levels is about $h(\tau_c)^{-1}$ where τ_c is the mean duration of the collision.

We here report the investigation of the magnetic field dependence of the collisional excitation transfer rate between the $J = 3/2$ $M = -3/2$ and $J = 3/2$ $M = 3/2$ Zeeman sublevels of the $3\,^2P_{3/2}$ state of Na, in Na–Na* resonant collisions.

The apparatus is described in a previous publication [8]. The resonance cell is placed at the center of a supraconductive magnet producing fields up to 80 kG. The cell is connected to a pumping line in order to avoid all the troubles due to residual gases which may severely perturb such experiments [1, 3]. The excitation of only one Zeeman substate is performed with a tunable jet stream dye laser [8]. The fluorescence light detected at right angles to the field direction is frequency analyzed with two thermostabilized piezoelectrically scanned Fabry Perot interferometers with adjustable mirror spacing. The free spectral ranges of the interferometers are chosen to get the least overlap of the Zeeman components on the 0–80 kG range of magnetic field [8]. For the study of the $-3/2 \rightarrow 3/2$ field dependance of the transfer rate, the free spectral ranges are chosen to be 2.65 cm^{-1} and 3.85 cm^{-1}.

The study of resonant collisions is always complicated by multiple scattering of resonance radiation [9, 10]. For strong fields (such that the Zeeman splitting is greater than the Doppler width and hyperfine structure), the Zeeman components of the lines are independently trapped in the vapour and multiple scattering does not produce any depolarization effects [1, 3, 11].

In the following, we assume that only one Zeeman sublevel m_0 is continuously laser excited and that the Zeeman splitting is greater than the Doppler width and the hyperfine structure of the lines ($B > 4$ kG). We also assume that ground state Na atoms are well described using an isotropic density matrix. This supposes that the relaxation processes are very rapid compared to the optical and collisional pumping rates of the ground state which is well verified in the experiments.

The rate equations for the population ρ_m of the excited states are then:

$$\dot{\rho}_m = 0 = -\left(\Gamma^{(m)} + \sum_{m'} g^{m'm}\right) \rho_m + g^{mm_0}\rho_{m_0}\,, \qquad (1)$$

* Fachbereich physik Universität Marburg, RFA.
* Associé au CNRS.

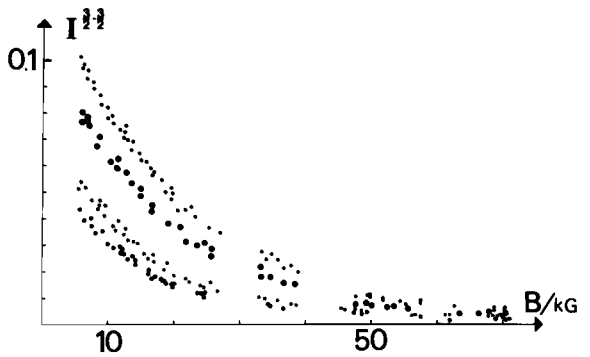

Fig. 1. Variations of $I^{3/2}/I^{-3/2}$ with the field at various sodium densities (•N = 4.2 × 10^{12} aT/cm^3, ☆ 3.8 × 10^{12}, ★ 3.3 × 10^{12}, ● 3.1 × 10^{12}).

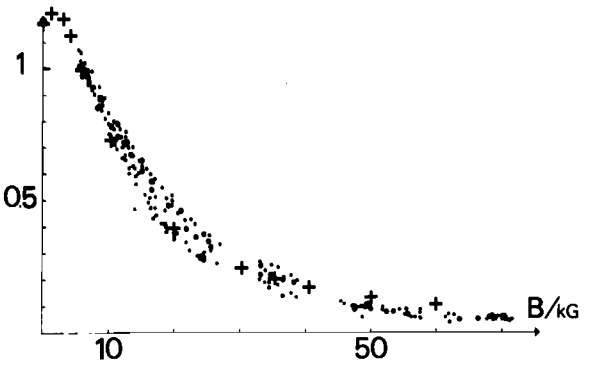

Fig. 2. Variations with the field of $\eta(B) = I^{3/2-3/2}(B)/I^{3/2-3/2}$ (6 kG). The theoretical values (+) are those estimated with the cut-off method.

$\Gamma^{(m)}$ is the inverse of the imprisonment time of the excitation in the m Zeeman sublevel and $g^{m'm}$ a mean collisional transfer rate from m to m'.

For the $-3/2 \rightarrow 3/2$ excitation transfer, $N = 2 \times 10^{12}$ at/cm^3 and $T = 500$ K, one may deduce from reference [12] that $g^{3/2-3/2} = 2.74 \times 10^{-3}\Gamma$ (Γ the radiative decay probability), the rates for the other processes being of the same order of magnitude. The imprisonment probability $\Gamma^{(3/2)}$ may be roughly estimated with the model of Holstein [13]. This gives $\Gamma/\Gamma^{(3/2)} \approx 27$. Under these conditions $\Gamma^{(3/2)} \gg \Sigma_{m'} g^{m'm}$.

The ratio of the fluorescence intensities may be expressed as [11]:

$$I_m/I_{m_0} = I^{mm_0} = \lambda(N)\rho_m/\rho_{m_0} \approx \frac{\lambda(N)}{\Gamma^{(m)}} g^{mm_0}, \qquad (2)$$

where $\lambda(N)$ depends on the distribution of the excitation in the cell. Formula (2) involves several approximations but gives reliable predictions till optical depths of about 30 as shown in experimental and theoretical investigations [1,3]. $\lambda(N)$ being in general no more than a few units [3], $I^{3/2-3/2}$ is about 0.07 at low field values for $N \approx 2 \times 10^{12}$ at/cm^3 which is in rather good agreement with the experimental data of fig. 1. With the above assumptions, *the ratio of the fluorescence intensities linearly depends on the g^{mm_0} transfer rate.*

The $J = 3/2$ $M = -3/2$ Zeeman sublevel is continuously laser excited. Particular attention has been paid to the excitation transfer towards the $J = 3/2$ $M = 3/2$ Zeeman sublevel, but of course results have been obtained for the other processes. Excitation transfer towards the $J = 1/2$ sublevels is still negligible small at the strongest (80 kG) field values but seems slightly increasing as expected. We have plotted on fig. 1 the ratio $I^{3/2-3/2}$ against the field. No measurements have been done around 30 and 42 kG and for field smaller than 6 kG because of line overlapping. Anyway, conceptual difficulties as mentioned above (multiple scattering and hyperfine structure) are existing at low fields.

In order to compare the variations with the field at different Na densities, we have normalized the results at the mean experimental value for $B = 6$ kG. This gives $\eta(B)$ such that:

$$\eta(B) = I^{3/2-3/2}(B,N)/I^{3/2-3/2}(6\,\text{kG},N) = g^{3/2-3/2}(B)/g^{3/2-3/2}(6\,\text{kG}). \qquad (3)$$

Then $\eta(B)$ does not depend on N within the experimental uncertainties as may be seen on fig. 2.

The dependence of the collisional transfer rate with the field strength which appears on fig. 2 is the most important one ever observed in resonant collisions [1,3,14]. The transfer in 70 kG fields is about 20 times smaller than the one at 6 kG. At strong fields, the saturation value is very weak and the contribution of R^{-3} dipole-dipole interaction to the excitation transfer which is essentially a long range contribution is almost disappearing. This also proves that the higher order non resonant terms of the potential are only weakly contributing to $-\frac{3}{2} \rightarrow \frac{3}{2}$ excitation transfer.

Very different field dependances have been observed for the other excitation transfer rates in Na-Na* collisions [3,14].

The analysis of Na–Na* (3^2P_J) resonant collisions taking into account the Larmor precession of the ground and excited states, $\boldsymbol{L}\cdot\boldsymbol{S}$ coupling and R^{-3} dipole-dipole interaction needs a numerical approach following the methods of [5], but requests a great amount of computer time. Moreover, no symmetry properties except rotational invariance in the $\boldsymbol{B}$ direction are expected to exist. Anyhow, for a $J=1\rightarrow J=0$ transition, the cut-off method developped by Omont [9] gives results which are for this particular kind of problems in general within 30% agreement with the numerical results [3]. Therefore we here use this method to estimate the variations and obtain some insight on the mechanism of the processes. The outline of the analysis which will be reported in greater details [14] is the following: a second order perturbation expansion of the relaxation matrix [3] taking into account $\boldsymbol{L}\cdot\boldsymbol{S}$ coupling, magnetic interaction and R^{-3} dipole-dipole interaction is performed. The angular averaged probability of excitation transfer $\Pi^{mm_0}(b, v, B)$ is then obtained [3, 14] and depends on the impact parameter b, on the velocity v and on the field strength B. The main problem is the determination of the strong collision mean value $\langle\Pi^{3/2-3/2}\rangle$ of $\Pi^{3/2-3/2}$. This is done using the exact numerically calculated values deduced from reference [12] in zero field and asserting that $\langle\Pi^{3/2-3/2}\rangle$ is a weakly varying function of B which is well verified for $J=1\rightarrow J=0$ transitions [3, 5]. We then deduce the cut-off radius b_c against the field [3, 9, 14] and the transfer rates $g^{mm_0}(B)$. For $-3/2\rightarrow 3/2$ excitation transfer, we obtain the set of implicit equations

$$\Phi(B)=g^{3/2-3/2}(B)/g^{3/2-3/2}(0)=\frac{1}{2}\frac{\eta^2}{\tau^2}\left(1+\frac{\tau^4}{\eta^4}F_1(2\eta)\right) \tag{4}$$

$$(\eta/\tau)^4=f_1(2\eta)\ \text{ with }\ \eta=\mu_B\cdot B\,b/v,\ \tau=0.106\,B(\text{kG}).$$

The $F_1(\eta)$ and $f_1(\eta)$ functions are combinations of modified K Bessel functions defined and tabulated in [3, 5, 9, 15].

The rate of variations of $g^{3/2-3/2}$ with the field is governed by $2\mu_B\cdot B$ and this needs some comments. At second order perturbation theory, four processes are contributing to the $m=-3/2\rightarrow m=3/2$ excitation transfer rate due to the two possible polarizations of the ground state perturbers before and after collision. As perturbers are unpolarized on the average and as we only detect the excitation transfer in the excited state, the mean transfer probability is obtained by summing over all the indices m_i refering to the ground state polarization: $\bar{\Pi}^{3/2-3/2}=\frac{1}{2}\Sigma_{m_1m_2}\Pi(-\frac{3}{2}m_1\rightarrow\frac{3}{2}m_2)$. The rate of variations with the field for the various contributing processes corresponds to internal energy conservation for the two atoms system. It is just $2\mu_B\cdot B|(m_2-m_1)+2|$ for $(-\frac{3}{2}m_1\rightarrow\frac{3}{2}m_2)$. So $\bar{\Pi}^{mm_0}$ is a priori depending on 4 different characteristic frequencies. But for $-3/2\rightarrow 3/2$ excitation transfer three processes are forbidden because of the electric dipolar selection rules obeyed by dipole-dipole interaction. The only term which is not zero corresponds to the $(-\frac{3}{2}m_1=\frac{1}{2}\rightarrow\frac{3}{2}m_2=-\frac{1}{2})$ process and $\Pi^{3/2-3/2}$ *evolves at only one characteristic frequency* which is $2\mu_B\cdot B$. Remark that if one neglects the role of the electronic spin of the ground state perturber in the collision we would have predicted a rate of variations with B corresponding to the splitting of the $-3/2$ and $3/2$ Zeeman sublevels i.e. $4\mu_B\cdot B$ which indeed refers to a strictly forbidden process here, but in Na*-rare gas collisions the only one [8]. Of course, in the general case, the use of polarized perturbers would allow to select only two among the four processes.

The theoretical values obtained form (4) are plotted on fig. 2 at $T=500$ K. The agreement with the experimental results is fairly good. It clearly shows that the rate of variations of $g^{3/2-3/2}$ is well described by $2\mu_B\cdot B$ and not with $4\mu_B\cdot B$ which would produce a faster decrease with the field.

The huge experimental field dependance experimentally observed illustrates the importance of collision time effects in resonant collisions. The good overall agreement with the theoretical model confirms both the importance of the role of selection rules and electronic spin in Na-Na* collisions and the long range character of the field action during the collision. The nearly complete elimination of the long range R^{-3} *contributions to excitation transfer at strong fields* suggests the possibility of studying the effects of the higher order non resonant terms of the potential which are masked in zero fields by the resonant contribution (about 8400 Å^2 for the $m=-3/2\rightarrow m=3/2$ excitation transfer cross section). The upper limit of 400 Å^2 which may be deduced from our results is yet fairly large compared to Na–Ne values [8] which give probably the order of magnitude of the non-resonant contributions in Na–Na* collisions. The extension of

such experiments in stronger fields (200 kG) would afford a study of the $m = -3/2 \rightarrow m = 1/2$ excitation transfer between fine structure sublevels through the crossing at 164 kG [3, 14].

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