J. Plasma Fusion Res. SERIES, Vol.7 (2006) 213-216

Broadening and Shifting of the Alkali-Metal Resonance Lines by Collisions of Like Monatoms

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(Received: 4 October 2004 / Accepted: 7 September 2005)

Abstract

The purpose of this work is the evaluation of the linewidth w and lineshift d of the sodium resonance line 3p $\longrightarrow$ 3s when the excited atoms are evolving in their parent gas. Assuming the Baranger impact approximation, these two quantities are given in terms of the phase shifts of the ground Na(3s) + Na(3s) and the excited Na(3p)+Na(3s) states. The quantal calculations and the semi-classical method, developed by Mott and Massey and Landau and Lifshitz, show that the cross sections σ and λ vary with the energy like $E^{-1/2}$, the width w and the shift d do not depend on the temperature, the long-range interactions have a big influence on w and d, and the rate coefficients depend on the dispersion coefficients like $w/n \approx +7.298 \times 10^{-8} C_3(\Sigma)$ and $d/n \approx +8.893 \times 10^{-9} C_3(\Sigma)$. The study also shows that the sodium results can be extended to the other alkali-metal atoms (Li, K, Rb, Cs, and Fr) by a simple scaling.

Keywords:

potential energy curve, broadening cross section, rate coefficient, linewidth, lineshift, dispersion coefficient

1. Introduction

The pressure broadening and shifting phenomena of a spectral line occur when an absorbing or emitting atom is perturbed by the atoms composing its gaseous environment. Besides the natural broadening, the line can be observed broadened symmetrically or asymmetrically and often accompanied by shift of the main frequency.

In the present study, we are interested in the evaluation of the width w and the shift d of sodium resonance line Na(3p $\longrightarrow$ 3s) when this radiating atom is interacting with Na(3s). The problem we consider here concerns the allowed singlet transitions only, namely $^1\Sigma_u^+ \longleftrightarrow X\ ^1\Sigma_g^+$ and $^1\Pi_u \longleftrightarrow X\ ^1\Sigma_g^+$. The former transition is denoted $\Sigma\Sigma$ and the latter $\Pi\Sigma$.

The singlet potential energy curves we have adopted for the calculations are presented in Fig. 1. The sodium ground and excited states, dissociating into 3s + 3s and 3p + 3s asymptotes, have been constructed by Côté and Dalgarno [1] and Bouledroua *et al.* [2], respectively. The leading terms in the long-range forms of both interactions are

$$V(R) \sim \begin{cases} -C_6/R^6, & \text{for Na(3s) + Na(3s)} \\ -C_3/R^3, & \text{for Na(3p) + Na(3s)} \end{cases} \qquad (1)$$

where, in atomic units, $C_6 = +1472$, $C_3(\Sigma) = +12.438$,

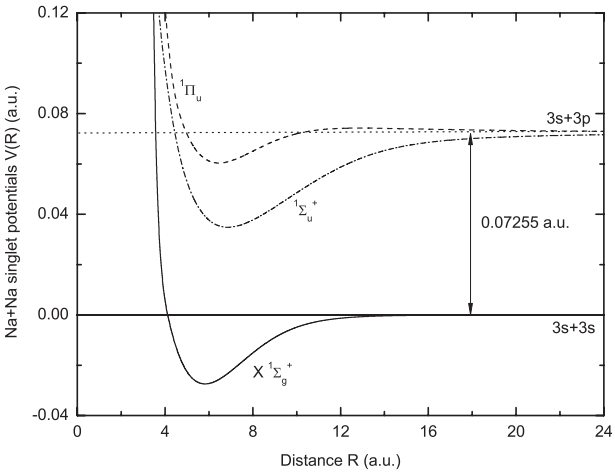

Fig. 1 The potential energy curves of the Na_2 molecular states involved in the singlet 3p $\longrightarrow$ 3s transitions.

and $C_3(\Pi) = -6.219$. These $X\ ^1\Sigma_g^+$, $^1\Sigma_u^+$, $^1\Pi_u$ potential curves are necessary to solve numerically the corresponding radial wave equation and, thus, to compute the phase shifts $\eta_l(E)$ at each energy E and angular momentum l.

Once the phase shifts are known, they permit to calculate quantum-mechanically the width and shift cross sections, σ and λ. The average cross section

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Q ($Q \equiv \sigma$ or $Q \equiv \lambda$) is simply the weighted sum

$$Q_{\text{singlet}} = \frac{1}{3} Q_{\Sigma\Sigma} + \frac{2}{3} Q_{\Pi\Sigma}. \qquad (2)$$

All the results below are in atomic units.

2. Baranger method

Assuming the impact approximation, and by treating quantum-mechanically the rectilinear motion of the perturbing atom, Baranger [3,4] found that the linewidth w and the lineshift d are given by

$$w = +n \langle v \cdot \sigma \rangle \qquad (3)$$

$$d = -n \langle v \cdot \lambda \rangle , \qquad (4)$$

where n is the gas density and v is the relative velocity. The symbol $\langle \cdots \rangle$ stands for the mean value calculated over a Maxwellian distribution.

The width and shift cross sections σ and λ are the sums [5]

$$\sigma = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2 \left(\eta'_l - \eta''_l \right) \qquad (5)$$

$$\lambda = \frac{\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin \left[2 \left(\eta'_l - \eta''_l \right) \right], \qquad (6)$$

$k = \sqrt{2\mu E}$ being the wave number, with μ the reduced mass of the radiator-perturber system. The phase shifts η'_l and η''_l correspond to the upper Na(3p) + Na(3s) and lower Na(3s) + Na(3s) states.

3. Quantum calculations

We have computed the total width and shift cross sections $\sigma(E) = \frac{1}{3}\sigma_{\Sigma\Sigma} + \frac{2}{3}\sigma_{\Pi\Sigma}$ and $\lambda(E) = \frac{1}{3}\lambda_{\Sigma\Sigma} + \frac{2}{3}\lambda_{\Pi\Sigma}$ correlated to singlet transitions. Figure 2 displays the case of σ variation with E.

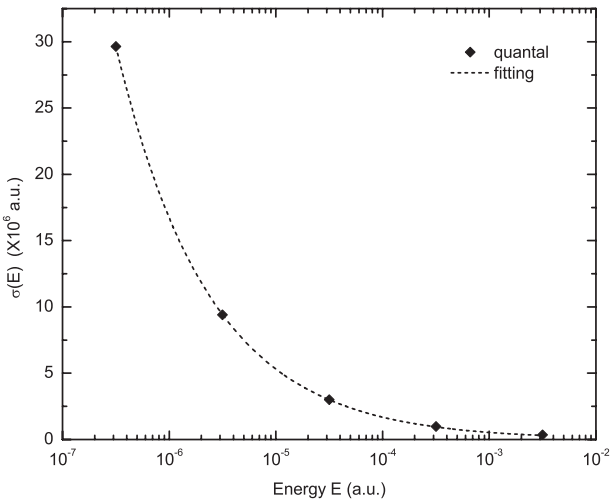

Fig. 2 Variation with energy of the width cross section σ (E). The dashed line represents the result of the fitting of our quantal data with the function $\sigma \sim aE^{\alpha}$.

We have further fitted both sets of data with the functions $\sigma \sim aE^{\alpha}$ and $\lambda \sim bE^{\beta}$. The constant parameters are found $\alpha = \beta \simeq -0.50$, $a \simeq 17220.35$, and $b \simeq -2010.63$. We conclude that both cross sections vary with energy like $1/\sqrt{E}$.

4. Semi-classical approximations

Since the values of l contributing in the expressions (5) and (6) are large, Mott and Massey [5] and Landau and Lifshitz [6] proposed a semi-classical method which consists to split the summation at a given angular momentum $l = L$, to replace the discrete sums by integrals, and to substitute, for large l, the quantal phase shifts by their asymptotic forms [5,7]

$$\eta'_l \approx \mu C_3 \frac{k}{l^2} \qquad (7)$$

$$\eta''_l \approx \left(\frac{3\pi\mu}{16} \right) C_6 \frac{k^4}{l^5}, \qquad (8)$$

with $\eta'_l \gg \eta''_l$.

For the case of σ, we get

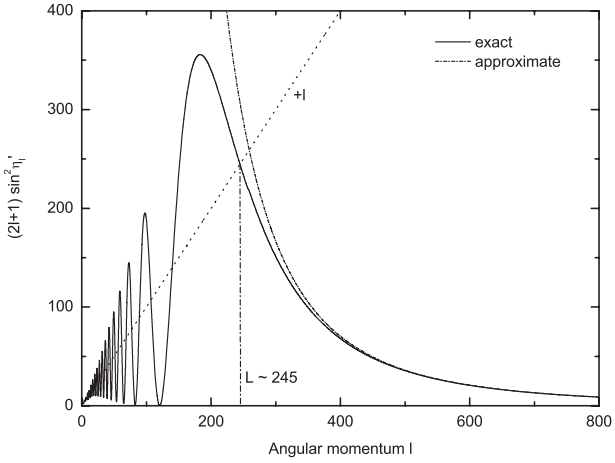

Fig. 3 Partial cross section, $(2l+1)\sin^2\eta'_l$, effective in width corresponding to the $\Pi\Sigma$ singlet transition at the energy $E = 10^{-5.5}$ a.u.

Table 1 The singlet width and shift cross sections (in 10^6 a.u.) obtained for $E = 1$ K by different methods.

Cross section	Quantal	Fitting	Semi-classical
σ	+9.397	+9.684	+8.529
λ	−0.943	−1.131	−1.039

Table 2 Singlet width and shift rate coefficients of alkali monatoms. The μ and C_3 constant values are from References given in [2].

Alkali metal	μ (a.u.)	C_3 (a.u.)	w/n (10^{-7}cm$^3\cdot$rad$\cdot$s^{-1})	d/n (10^{-7}cm$^3\cdot$rad$\cdot$s^{-1})
^{7}Li	6326.33	11.00	8.028	0.978
^{23}Na	20953.89	12.44	9.077	1.106
^{39}K	35635.92	16.89	12.33	1.502
^{85}Rb	77899.13	17.88	13.05	1.590
^{133}Cs	121135.89	20.10	14.67	1.788
^{210}Fr	203252.07	17.69	12.91	1.573

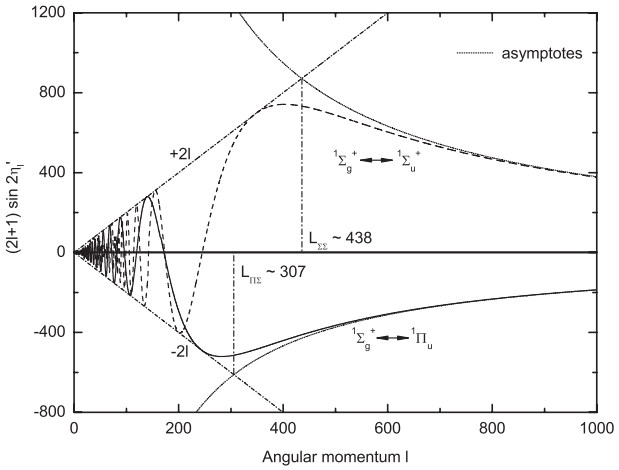

Fig. 4 Partial cross section, $(2l+1)\sin 2\eta_l'$, effective in shift corresponding to the $\Sigma\Sigma$ and $\Pi\Sigma$ singlet transitions at the energy $E = 10^{-5.5}$ a.u.

$$\sigma \approx \frac{4\pi}{k^2}\int_0^L 2l\sin^2\eta_l' dl + \frac{4\pi}{k^2}\int_L^\infty 2l\sin^2\eta_l' dl. \quad (9)$$

The cut-off value L is obtained from the approximation $\sin^2\eta_{l=L}' \simeq 1/2$. Making use of Eq. (7), we find

$$L \simeq \left[\frac{2}{\pi}(2\mu)^{3/2}\,|C_3|\,\sqrt{E}\right]^{1/2}. \quad (10)$$

Knowing $C_3(\Sigma) = 2\,|C_3(\Pi)|$, the calculations lead to the semi-classical expression

$$\sigma(E) \approx \frac{1}{3}\left(8+\pi^2\right)C_3(\Sigma)\sqrt{\frac{2\mu}{E}} \equiv \frac{a}{\sqrt{E}}. \quad (11)$$

Numerically, $2\mu = 41907.79, C_3(\Sigma) = +12.438$, and $a \simeq 15166.70$; for $E = 1\,\mathrm{K} \approx 10^{-5.5}$, we find $L \simeq 245$. Figure 3 illustrates this numerical result for the case of the $\Pi\Sigma$ transition. The weighted values of $\sigma(E)$ at this energy are given in Table 1. The results obtained by different approaches are very close.

When applying the same technique to the shift cross section λ, the second term corresponding to $l > L$ diverges. To overcome this divergence, one has to apply the procedure on the weighted sum $\lambda(E) = \frac{1}{3}\lambda_{\Sigma\Sigma} + \frac{2}{3}\lambda_{\Pi\Sigma}$. By doing so, the semi-classical method yields the approximate formula

$$\lambda(E) \approx -\frac{2\pi}{3}C_3(\Sigma)\ln\left(\frac{L_{\Sigma\Sigma}}{L_{\Pi\Sigma}}\right)\sqrt{\frac{2\mu}{E}} \equiv \frac{b}{\sqrt{E}} \quad (12)$$

where $L \simeq \sqrt{2\mu\,|C_3|\,k}$ and $L_{\Sigma\Sigma}/L_{\Pi\Sigma} \simeq \sqrt{2}$. Table 1 lists our results obtained for $E = 1$ K by different methods. The agreement is excellent. We also report in Fig. 4 the partial shift cross sections, $(2l+1)\sin 2\eta_l'$, relative to the $\Sigma\Sigma$ and $\Pi\Sigma$ transitions at the same energy. The straight lines $\pm 2l$ come from the fact that, for $l < L$, the sine function lies between -1 and $+1$.

It is interesting to point out that the semi-classical method shows explicitly the influence of the long-range forces, via the dispersion coefficients C_3, on the width and shift cross sections, hence on the spectral linewidth and lineshift.

5. Statistical average

We have found that both cross sections obey the general formula $Q(E) \simeq A/\sqrt{E}$, with A a constant. Supposing a Maxwellian distribution, it is easy to get

$$\langle v\cdot Q\rangle \simeq A\sqrt{\frac{2}{\mu}}. \quad (13)$$

From the expressions (3) and (4), we notice that the width w and the shift d do not depend on temperature T. The singlet rate coefficients, in cm$^3\cdot$rad$\cdot$s^{-1}, are given by

$$\frac{w}{n} \sim +7.298\times 10^{-8}\,C_3(\Sigma) \quad (14)$$

$$\frac{d}{n} \sim +8.893\times 10^{-9}\,C_3(\Sigma), \quad (15)$$

the density n being in cm^{-3}.

For Na resonance line, the computation yields $w/n \simeq 9.077 \times 10^{-7}\ \mathrm{cm}^3 \cdot \mathrm{rad} \cdot \mathrm{s}^{-1}$ and $d/n \simeq 1.106 \times 10^{-7}\ \mathrm{cm}^3 \cdot \mathrm{rad} \cdot \mathrm{s}^{-1}$. When compared to quantum-mechanical results, these singlet width and shift rates are respectively 12 % and 8 % smaller.

From the above relations, one may notice that the linewidth and lineshift are exclusively given in terms of the dispersion coefficient C_3. It is therefore possible to deduce the values of the rate coefficients for the other alkali metals just by a simple scaling. Their estimated data are presented in Table 2.

Acknowledgements

A part of this work has already been published (Ref. [2]). It was supported by the National Science Foundation through the ITAMP.

References

[1] R. Côté and A. Dalgarno, Phys. Rev. A **50**, 4827 (1994).

[2] M. Bouledroua, A. Dalgarno and R. Côté, Phys. Rev. A **65**, 012701 (2001).

[3] M. Baranger, Phys. Rev. **111**, 481 (1958).

[4] J. Szudy and W.E. Baylis, J. Quant. Spectr. Radiat. Transf. **15**, 641 (1975); Phys. Rep. **266**, 127 (1996).

[5] N.F. Mott and H.S.W. Massey, *The Theory of Atomic Collisions* (Oxford University Press, Oxford, 1965).

[6] L.D. Landau and E.M. Lifshitz, *Quantum Mechanics, Non-Relativistic Theory* (Pergamon Press, Oxford, 1981).

[7] A. Dalgarno, M.R.C. McDowell and A. Williams, Philos. Trans. R. Soc. Lond. A **250**, 411 (1958).