Calculation of Line Broadening Cross Sections for Level Crossing Experiments in Alkali-Rare Gas Systems

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Using a simple approximation for the theoretical atomic interaction constants cross section data for level crossing and Hanle-effect line broadening experiments in Rb, Mg^+ and Ca^+ rare gas systems could be derived. It is shown that in the Rb system the interaction $C_6 R^{-6}$ is predominant and that the results are little influenced by dipole-quadrupole and repulsive interactions in the frame work of the Lindholm-Foley-Hindmarsh theory.

1. Introduction

Spectral line broadening gives information on the interaction between the radiating system in its upper and lower state and the collision partner. Some time ago the line broadening of transitions of atoms and ions with one valence electron by rare gas atoms in the ground state was measured using Hanle-effect (zero field level crossing) and level crossing techniques[1, 2].

These modern spectroscopic methods are appealing for the following reasons:

a) the measurements can be performed at low pressures of radiating and perturbing atoms thus allowing only two-body collisions,
b) there is no Doppler-broadening,
c) the raising of foreign gas pressure enables the formation and observation of molecular complexes,
d) in the interaction of ions with atoms the statistical Stark-broadening can be avoided.

A disadvantage is that only the broadening but no shift can be observed. This is the reason why only one interaction constant can be derived from the experimental cross section values. If there are more than one interaction constants involved it is only possible to test theoretical constants by comparing the experimental cross section data with those derived from theoretical considerations.

As the formal theories of line broadening[3, 4], especially for the Hanle-effect[5], are too difficult to apply to experiments, we used the Hindmarsh generalization of the Lindholm-Foley theory[6] including higher order attraction and repulsive interactions. It will be shown that the Lindholm-Foley theory gives the right order of broadening cross section values for level crossing signals of neutral atoms and ions with one valence electron perturbed by rare gases.

As Hindmarsh[6] gives an excellent review on the collision broadening of spectral lines by neutral atoms this paper is organized as follows: Part 2 gives the relevant formulae of the Lindholm-Foley-Hindmarsh theory; in Part 3 the necessary atomic constants are calculated and Part 4 relates experimental and theoretical cross section data which are discussed in Part 5.

2. Summary of the Lindholm-Foley-Hindmarsh Theory

The interaction potential $V(R)$ between two atoms, one atom in an S-state, has the form

$$V(R) = C_n R^{-n} - C_8 R^{-8} - C_6 R^{-6} . \qquad (1)$$

$C_6 R^{-6}$ is the dipole-dipole-, $C_8 R^{-8}$ the dipole-quadrupole- and $C_n R^{-n}$ a quantum mechanical repulsion term whose parameter n can be 10 or 12 as will be discussed later. Assuming the potential Eq. (1) for the ground- and the excited state of the radiating system and the perturbing atom the potential difference written as angular frequency is:

$$\Delta\omega = C_n^* R^{-n} - C_8^* R^{-8} - C_6^* R^{-6} \qquad (2)$$

with

$$C_m^* = (C_m^{\text{exc}} - C_m^{\text{ground}})/\hbar , \quad m = n, 6, 8 . \qquad (3)$$

The phase change $\eta(\varrho)$ caused by a collision of impact parameter ϱ and average relative velocity $\bar{v}$ can be calculated by standard integration, yielding:

$$\eta(\varrho) = \alpha_n x^{-(n-1)} - \beta x^{-7} - x^{-5} \qquad (4)$$

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with

$$x = \varrho \left[\frac{3\pi}{8}\,\frac{|C_6^*|}{\bar{v}}\right]^{-1/5} \tag{5}$$

and

$$\bar{v} = \sqrt{\frac{8RT}{\pi}\left(\frac{1}{M_1}+\frac{1}{M_2}\right)}, \tag{5 a}$$

where R is the gas constant, T is the absolute temperature, and M_1, M_2 are the atomic masses of the colliding particles,

$$\alpha_{12} = (63\,\pi/256)\,(8/3\,\pi)^{11/5}\,\bar{v}^{6/5}\,|C_{12}^*|/|C_6^*|^{11/5}, \tag{6}$$

$$\alpha_{10} = (35\,\pi/128)\,(8/3\,\pi)^{9/5}\,\bar{v}^{4/5}\,|C_{10}^*|/|C_6^*|^{9/5}, \tag{7}$$

$$\beta = (5\,\pi/16)\,(8/3\,\pi)^{7/5}\,\bar{v}^{2/5}\,|C_8^*|\,|C_6^*|^{-7/5}. \tag{8}$$

The damping constant or half half-width γ caused by the collision is given by Eq. (9), where N is the density of the perturbing gas:

$$\gamma = 4\,N\,\pi\,(3\,\pi/8)^{2/5}\,\bar{v}^{3/5}\,|C_6^*|^{2/5}\,B(\alpha_n,\beta) \tag{9}$$

with

$$B(\alpha_n,\beta) = \int_0^\infty x\sin^2\{0{,}5\,(\alpha_n x^{-(n-1)} - \beta x^{-7} - x^{-5})\}\,\mathrm{d}x\,. \tag{10}$$

This integral was evaluated numerically for a wide range of constants α_n, β and is given in the Fig. 1 and 2.

The interaction constants will be calculated semi-empirically in the following part.

3. Calculation of Atomic Interaction Constants

3.1 Dipole-dipole Van der Waals constant C_6

Mahan[7] showed that C_6 can be calculated for systems with one valence electron by a combination of dipole polarizabilities of the rare gas atoms and expectation values of powers r^k (k = integer) for the alkali-like particles were $\boldsymbol{r}$ is the coordinate of the valence electron. He used the simple approximation for hydrogenic orbitals with an effective radial quantum number $n^* = Z\sqrt{R_\infty/T}$, where $R_\infty = 109737{,}31\ \mathrm{cm}^{-1}$ is the Rydberg constant, T is the term value[8], and Z is the effective atomic charge, 1 for neutral atoms, 2 vor singly ionized atoms.

We used his results for the Rb-$6^2\,\mathrm{P}_{3/2}$-level and calculated the constants for the Mg^+-$3^2\,\mathrm{P}_{3/2}$- and Ca^+-$4^2\,\mathrm{P}_{3/2}$-levels in the same way.

The relevant formulae[7], appropriate for the use of SI-units are:

$$|C_6(l)| = \{e/(4\,\pi\,\varepsilon_0)\}^2\,\alpha_\mathrm{D}\,\langle r^2\rangle\,, \tag{11}$$

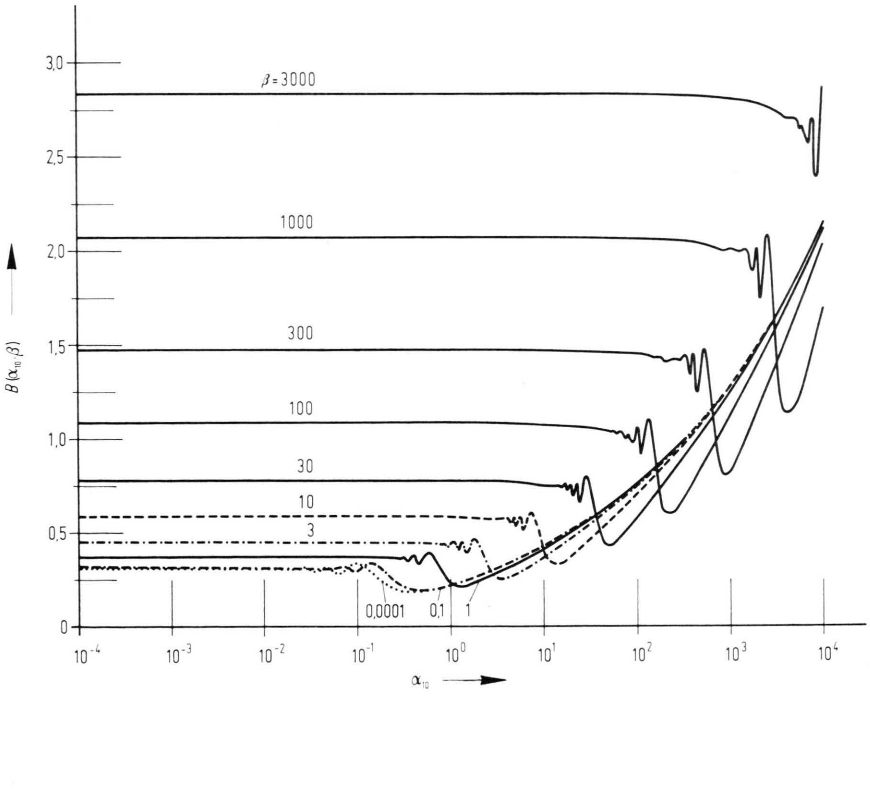

Fig. 1. Integral $B(\alpha_{10},\beta)$ as a function of the parameters α_{10} and β.

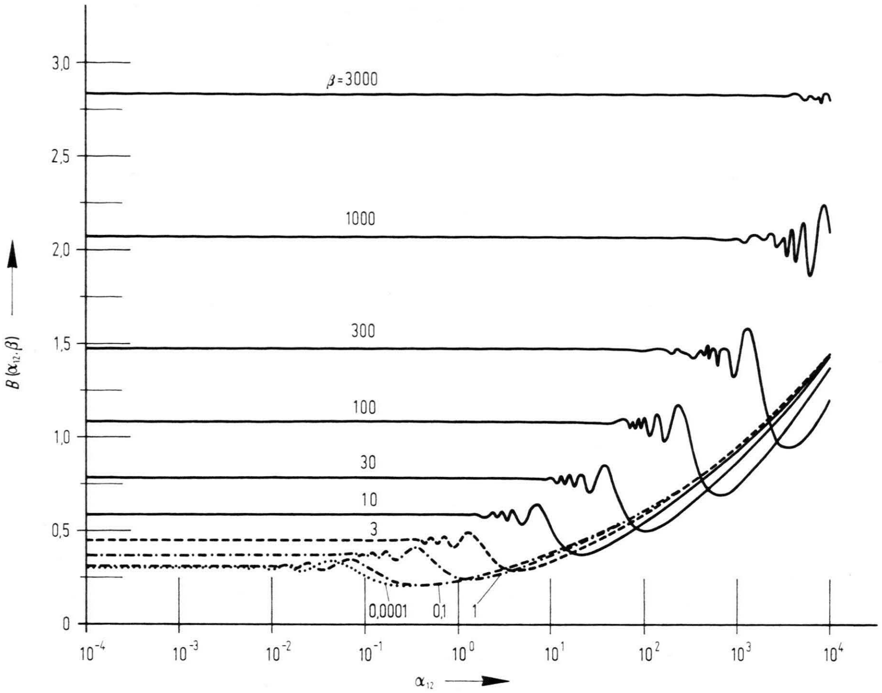

Fig. 2.
Integral $B(\alpha_{12}, \beta)$ as a function of the parameters α_{12} and β.

$$\langle r^2 \rangle = (1/2)\, a_0^2 (n^*/Z)^2 [5\, n^{*2} + 1 - 3\, l(l+1)] \,, \tag{12}$$

$$\langle r^4 \rangle = (1/8)\, a_0^4 (n^*/Z)^4 [63\, n^{*4} + 12 - 35\, n^{*2} (2\, l^2 + 2\, l - 3) + 5\, l\, (l+1)\, (3\, l^2 + 3\, l - 10)] \,. \tag{13}$$

$a_0 = 0{,}529167 \cdot 10^{-10}$ m is the Bohr radius, $e = 1{,}60210 \cdot 10^{-19}$ As is the electron charge, $\varepsilon_0 = 8{,}85419 \cdot 10^{-12}$ As V^{-1} m^{-1} is the influence constant, l is the angular momentum quantum number, α_D is the dipole polarizability of the rare gas atoms in As m^2 V^{-1}. The hydrogenic wavefunctions are a good approximation to the asymptotic expansion of Whittaker-functions used by Davison[9].

In the case of the atom-ion collision an additional potential term $-C_4/R^4$ exists due to the interaction between the ionic charge and the charge induced dipole moment in the rare gas atoms. But because the interaction constant C_4 for an ion being in the ground state is the same as for an ion being in the excited state, the line broadening, depending only on the potential difference $\Delta\omega$, is not influenced by this interaction. However, for the Mg$^+$, Ca$^+$ rare gas system we multiplied the C_6-constants calculated with the formulae above with a factor of 2 following Smith and Gallagher[1].

3.2 The dipole-quadrupole-interaction constant C_8^*

C_8^* can be approximated by[10]:

$$|C_8^*| = e^2\, \hbar^{-1} (4\, \pi\, \varepsilon_0)^{-2} [\alpha_D (\langle r^4_{\text{exc}} \rangle - \langle r^4_{\text{ground}} \rangle) + (5/2)\, \alpha_Q (\langle r^2_{\text{exc}} \rangle - \langle r^2_{\text{ground}} \rangle)] \,, \tag{14}$$

where $\langle r^4 \rangle$ and $\langle r^2 \rangle$ may be calculated using Eqs. (12) or (13) respectively. The quadrupole polarizabilities α_Q of the perturbing gases (not to be confused with the abbreviation α in Part 2) are calculated by a statistical perturbation method using Hartree-Fock densities[11].

A comparison with the best available values from coupled Hartree-Fock calculations for He[12], Ne[13] and Ar[14] shows good agreement, so that the results for Kr are reliable.

3.3 The short range repulsion constant C_n

Short range repulsion in overlapping electron distributions is caused by the Pauli-principle and can therefore be calculated by quantum mechanical methods only. Though there has been great progress in the ab initio calculation of molecular potentials[15] the number of molecular systems is limited because of the long computation times. Semiempirical and empirical values of the interaction constant are applied to the calculation of the repulsive influence on spectral line-broadening. Hindmarsh, assuming a Lennard-Jones-type interaction $\sim R^{-12}$, gave a prescription for the calculation of C_{12} from atomic densities. We followed his method and calculated the necessary effective atomic radii. To get an estimation of the order of magnitude of the C_{12} constant we assumed, following Hindmarsh[6], that $C_{12} = q\, R_0^{12}$, where q is a constant, $R_0 = R_1 + R_2$ and R_1, R_2 are the radii of the atoms 1 and 2. To define R_1 and R_2 the radial charge density of $0{,}012\, e/a_0^3$ is used. We calculated the charge densities for the rare gases from Hartree-Fock or Hartree-Fock-Slater wavefunctions. For the one valence electron systems the Coulomb-approximation is used.

For the constant q a value of $(0{,}9 \pm 0{,}3) \cdot 10^{-23}\, J$ gives the best agreement with the experiment[6].

The interaction $\sim R^{-12}$ is not free from experimental objections. Recent atomic beam measurements suggest much softer potentials for the rare gases $\sim (R^{-8})$ to (R^{-10})[16] and an even softer potential $\sim R^{-7}$ for the K-Ar and K-Xe-groundstate interaction[17]. We calculated the integral Eq. (10) for a potential $\sim R^{-10}$, which seems to be a better approximation but which lacks from a method of calculating the constant C_{10}. To estimate the order of magnitude we calculated the groundstate C_{10} constants with a $10-6$-potential from Baylis'[18] semiempirical well depth and equilibrium distance and multiplied it with the factor which related the ground- and excited C_{12}-values by Hindmarsh's method.

Furthermore the short range repulsion is complicated by several ways of forming a quasimolecular state between the excited atom in a P-state and the rare gas atom in the groundstate. According to the Wigner-Witmer-rules they can combine to $^2\Sigma$-, $^2\Pi$-states which can be attractive or repulsive.

All atomic constants are given in Table 1 and the interaction constants in Table 2. We have calculated the interaction constants for the temperatures $T = 353$ K in the Rb system[2] and $T = 413$ K in the Mg^+ and Ca^+ system[1].

4. Interpretation of Level Crossing and Hanle-effect Measurements

Following Hindmarsh[6] the line broadening cross section σ is related to the full line width 2γ caused by a collision by

$$2\gamma = 2 N \bar{v} \sigma . \qquad (15)$$

	α_D	α_Q	α_Q[11]	R	$\langle r^2 \rangle$	$\langle r^4 \rangle$	n^*
He	0,23[19]	0.108[12]	0,105	1,77	0,42	0,61	—
Ne	0,44[19]	0.300[13]	0,33	2,02	2,63	2,13	—
Ar	1,83[19]	2.18[14]	2,4	2,72	7,26	11,3	—
Kr	2,76[19]	—	4,1	3,0	11,05	19,2	—
Xe	4,50[19]	—	9,1	4,0	16,2	31,6	—
Mg^+	6,2[11]	—	—	3,4	2,417	9,757	1,9025
$Mg^+ (3^2P_{3/2})$	—	—	—	4,8	3,711	23,417	2,2657
Ca^+	12,4[11]	—	—	4,2	3,836	23,366	2,1411
$Ca^+ (4^2P_{3/2})$	—	—	—	5,7	5,720	52,602	2,4982
Rb	48,7[19]	—	—	5,7	7,878	106,19	1,8048
$Rb (6^2P_{3/2})$	—	—	—	17,8	78,228	8814,94	3,3296

Table 1. Atomic constants calculated according to the formulas of the text.

α_D = dipole polarizability in 10^{-40} Asm²/V;
α_Q = quadrupole polarizability in 10^{-60} Asm⁴/V;
R = atomic radius in 10^{-10} m;
$\langle r^2 \rangle$ = average of r^2 in 10^{-20} m²;
$\langle r^4 \rangle$ = average of r^4 in 10^{-40} m⁴;
n^* = effective radial quantum number.

		$\lvert C_6^* \rvert$	$\lvert C_8^* \rvert$	$\lvert C_{10}^* \rvert$	$\lvert C_{12}^* \rvert$
$Rb (6^2P_{3/2})$	—He	318,33	39,796	7,9928	26,933
	—Ne	608,98	76,578	32,222	31,364
	—Ar	2532,8	322,05	13,269	47,568
	—Kr	3820,0	487,38	12,195	55,968
	—Xe	6228,2	802,99	9,2664	98,321
$Mg^+ (3^2P_{3/2})$	—He	11,703	0,068527	—	$5{,}2093 \cdot 10^{-5}$
	—Ne	22,388	0,13931	—	$8{,}0934 \cdot 10^{-5}$
	—Ar	93,115	0,64474	—	$25{,}557 \cdot 10^{-5}$
	—Kr	140,44	1,0030	—	$39{,}254 \cdot 10^{-5}$
	—Xe	228,97	1,7889	—	$161{,}06 \cdot 10^{-5}$
$Ca^+ (4^2P_{3/2})$	—He	17,057	0,14211	—	$24{,}016 \cdot 10^{-5}$
	—Ne	32,631	0,28383	—	$35{,}385 \cdot 10^{-5}$
	—Ar	135,72	1,2757	—	$98{,}086 \cdot 10^{-5}$
	—Kr	204,69	1,9686	—	$143{,}92 \cdot 10^{-5}$
	—Xe	333,73	3,4335	—	$513{,}30 \cdot 10^{-5}$

Table 2. Interaction constants calculated according to the formulas of the text.

C_6^* = dipole-dipole interaction constant in 10^{-45} m⁶ s⁻¹;
C_8^* = dipole-quadrupole interaction constant in 10^{-62} m⁸ s⁻¹;
C_{10}^* = interaction constant from the quantum mechanical repulsion term with $n=10$ in 10^{-76} m¹⁰ s⁻¹;
C_{12}^* = interaction constant from the quantum mechanical repulsion term with $n=12$ in 10^{-95} m¹² s⁻¹.

Combining Eq. (9) and Eq. (15) one gets the following relation between the cross section and the atomic interaction constants:

$$\sigma_n = 4\,\pi\,(3\,\pi/8)^{2/5}(|C_6{}^*|/\bar{v})^{2/5}\,B(\alpha_n,\beta)\,. \qquad (16)$$

As only one interaction constant can be derived from experimental line widths the interpretation of level crossing measurements is difficult. In conventional line broadening experiments the shift of the spectral line can be observed leading to two parameters deducable from the experiment.

We, therefore, did not try to deduce the interaction constants from the experimental data, but tried to answer the question, whether it is possible to get cross section data of the right order from the theoretical approximations given in the text.

Using Eq. (16) together with the calculated interaction constants and the appropriate values of $B(\alpha_n, \beta)$ taken from the figures we got the theoretical cross section data σ_{10}, σ_{12} and σ_0, which are summarized in Table 3. σ_{10} and σ_{12} are the cross section data taking a short range repulsion into account and σ_0 is the cross section value neglecting this quantum mechanical interaction and C_8.

Table 3. Theoretical and experimental cross section data.
σ_{10} = theoretical cross section for a repulsion term of the order $n=10$ in 10^{-18} m^2,
σ_{12} = theoretical cross section for a repulsion term of the order $n=12$ in 10^{-18} m^2,
σ_0 = theoretical cross section neglecting the quantum mechanical repulsion term and $C_8{}^*$ in 10^{-18} m^2,
σ_{exp} = experimental cross section from Hanle-effect and level crossing experiments in 10^{-18} m^2.

		σ_{10}	σ_{12}	σ_0	σ_{exp}
Rb ($6^2P_{3/2}$)	–He	11,9	8,6	2,3	4,3 [2]
	–Ne	12,7	9,8	4,0	—
	–Ar	11,8	10,7	7,8	6,6 [2]
	–Kr	11,7	10,6	10,1	10,3 [2]
	–Xe	11,9	11,7	12,8	—
Mg$^+$ ($3^2P_{3/2}$)	–He	—	0,7	0,6	—
	–Ne	—	0,8	1,0	—
	–Ar	—	1,4	1,8	1,3 [1]
	–Kr	—	2,2	2,2	—
	–Xe	—	2,5	2,7	—
Ca$^+$ ($4^2P_{3/2}$)	–He	—	1,0	0,7	—
	–Ne	—	1,1	1,2	—
	–Ar	—	1,6	2,2	1,4 [1]
	–Kr	—	2,5	2,8	—
	–Xe	—	2,9	3,4	—

5. Discussion of the Calculated Data

Comparing the calculated cross section data σ_{10} and σ_{12} with the values σ_{exp} evaluated from Hanle-effect and level crossing experiments [1, 2] one can see that the theoretical data are too high in the Rb rare gas system systematically, but have the right order despite the rough approximation procedure described in the text, especially for the C_{10} interaction constant. The rather good agreement of σ_0 with the experimental values seems to show that in the Rb rare gas system the interaction $C_6 R^{-6}$ is predominant and that the results are little influenced by dipole-quadrupole and repulsive interaction.

In the Mg$^+$ and Ca$^+$ rare gas system there is a very good agreement between the calculated σ_{12} values and the experimental one.

In conclusion, one can say that the Lindholm-Foley-Hindmarsh theory seems to be a very simple tool to evaluate cross section data of the right order for the line broadening of alkali are gas systems in Hanle-effect and level crossing experiments.

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