Application of the Model Microfield Method to Stark Profiles of Alkali Metal Resonance Lines

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Z. Naturforsch. **33a**, 1575–1580 (1978); received August 4, 1978

Stark widths and shifts of alkali metal resonance lines are calculated by the model microfield method (MMM). The impact results of Griem for the prevailing electronic broadening are recovered by the unified MMM. Both theories are in close agreement with recent experimental results. It is shown further that the shift values are very sensitive to the line strength values of the involved transitions. The reliability of the experimentally observed regularities through the alkali sequence is next discussed. On the basis of the MMM results these regularities can be understood in terms of the line strengths and frequencies of transitions from the main levels actually involved.

I. Introduction

First measurements of Stark broadened resonance lines of the alkali metals LiI, NaI, KI and RbI have been recently published [1, 2]. The calculation of the Stark widths and shifts of these isolated lines raises some questions of theoretical interest: impact or static character of the ionic broadening [3, 4, 5], importance of a quadrupolar contribution [4], limit of validity of some semi-classical calculations due to the important role played by strong fields in the electronic broadening [5]. The existing semi-classical theories do not agree concerning the two first points and therefore a confrontation between the various calculations and experiments seems fruitful.

On the other hand, the similarity of the outer shell configurations of the homologous alkali metal atoms can give regularities for Stark parameters of analogous transitions [6, 7, 8]. However, the unexpected behaviour (particularly for the LiI shift) observed in the mentioned experiment calls for a more precise appreciation of the correct influence of the various atomic quantities involved in the broadening mechanism.

In Sect. II, after a brief recall of the Model Microfield Method (MMM) principles, we discuss its results in comparison with other theories. Notwithstanding drastic differences in the treatment of ionic broadening, the impact results of Griem [3] for the prevailing electronic broadening are recovered by the MMM without any approximation, as a consequence of the internal consistency of this unified theory. In Sect. III, we present a critical comparison with experiment, emphasizing the existence of not negligible theoretical uncertainties in the shift calculations related to the rather poor accuracy achieved on the line strength values. Finally, in Sect. IV, we discuss the observed regularities of Stark parameters through the alkali sequence. We propose also a dependence of widths and shifts on an appropriate combined atomic quantity which accounts for the "irregular" negative shift of the LiI line.

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II. Theory

II.1. General Features of the MMM Applied to Isolated Lines

The MMM has been described in previous papers [9, 10, 11, 5]. We recall here briefly the main features of this semi-classical theory.

Instead of looking for approximate solutions of the Schrödinger equation for the actual plasma microfield, the MMM gives an exact solution for a model microfield having the same main statistical properties as the actual field: the probability distribution of the time-averaged field (which involves the instantaneous probability distribution), the weak field covariance, the interval between strong fields and the duration of these strong fields. As discussed in Brissaud and Frisch [9, 10], the

MMM is not afflicted with divergencies at short or large impact parameters and recovers as limiting cases the usual impact and static approximations. So the MMM constitutes unified theory already applied in a wide range of physical conditions to hydrogen, overlapping helium and isolated neutral lines.

For an isolated line corresponding to a transition between an initial level (i) and a final level (f), the auto-correlation function $C(t)$ (whose Fourier-Transform gives the line profile) reduces to:

$$C(t) = |\langle f|\, \boldsymbol{d}\, |i\rangle|^2 \{\langle f|\, T\, |f\rangle \langle i|\, T^+\, |i\rangle\}\, \varrho_i \quad \text{(II.1)}$$

where $\{\cdots\}$ denotes an average over perturber positions and motion, $\boldsymbol{d}$, ϱ and T are respectively the dipole moment, the density matrix and the time evolution operator of the radiator. For the lines investigated here the perturbation of the lower level is not negligible and the calculation of the second order moment of the radiator evolution operator $U = T \otimes T^+$ is required (Baranger [12]).

U satisfies an equation which can be deduced element by element from the equation

$$\begin{cases} \dfrac{\mathrm{d}}{\mathrm{d}t}\, T \otimes T^* = M[\boldsymbol{E}(t)]\, T \otimes T^*\,, \\ T(t',t') \otimes T(t',t') = I\,, \\ M = -\dfrac{i}{\hbar}(H_0 + V) \otimes I + \dfrac{i}{\hbar} I \otimes (H_0 + V) \end{cases} \quad \text{(II.2)}$$

where T^* is the complex conjugate of T, I the identity operator, H_0 the Hamiltonian of the unperturbed radiator and $V(t) = -\boldsymbol{E}(t) \cdot \boldsymbol{d}$ the interaction Hamiltonian. $\boldsymbol{E}(t)$ is the electric microfield of the plasma. The exact solution of Eq. (II.2) is formally given by the direct application of Eq. (17) established by Brissaud and Frisch [9] (substituting $U = T \otimes T^+$ in place of T) for the total (electronic plus ionic) model microfield.

However, this would lead to rather complex calculations. It has been shown (Brissaud et al. [11]) that a separate treatment of the electronic and ionic fields, and the convolution of the two resulting profiles is a satisfactory approximation for isolated lines and yields a considerable simplification. Some more details on the method and the numerical procedures (calculation of the mean static resolvent, strong fields treatment) can be found in Brissaud et al. [5].

Table 1. Some characteristic parameters of the alkali-metal resonance lines ($N = 10^{17}$ cm^{-3}; $T = 2 \cdot 10^4$ K). K_c is the collective Kubo number, $\beta^* = (r_0/r^*)^2$ is the electronic critical field and a_0 and $\lambda\!\!\!^{-} = \hbar/mv$ are the Bohr radius and the De Broglie wavelength of the perturbers, respectively.

	LiI 2s–2p	NaI 3s–3p	KI 4s–4p	RbI 5s–5p	CsI 6s–6p
Electrons					
K_c	$3.0 \cdot 10^{-5}$	$7.0 \cdot 10^{-5}$	$1.5 \cdot 10^{-4}$	$2.0 \cdot 10^{-4}$	$3.0 \cdot 10^{-4}$
β^*	1800	1050	650	500	380
$r^*/n^2 a_0$	1.5	0.9	0.6	0.5	0.4
$r^*/\lambda\!\!\!^{-}$	1.5	2	2.5	3	3.5
Ions (Ar^+)					
K_c	$3.0 \cdot 10^{-3}$	$1.1 \cdot 10^{-2}$	$2.7 \cdot 10^{-2}$	$4.5 \cdot 10^{-2}$	$7.5 \cdot 10^{-2}$

II.2. Application to Alkali-Metal Resonance Lines

As shown in Table 1, the resonance lines of the alkali-metal atoms present very similar features. Let us briefly recall the essential signification of the parameters K_c and β^* appearing in this table. The collective Kubo number K_c ($\gg 1$ or $\ll 1$) decides whether the profile is static or impact; β^* is a critical field ($\beta = E/E_0$, E_0 being the typical field): the width of an impact profile is essentially determined by the fields $\beta < \beta^*$ (Brissaud et al. [11]*.) Table 1 shows that in the considered range of physical conditions, both the electronic and the ionic Kubo numbers are much smaller than unity, essentially due to the large energy separation between the atomic levels. This leads to impact profiles for which strong fields are predominant.

We must stress that the impact character of ionic profiles, as already pointed out by Sahal-Bréchot [4] and Brissaud et al. [5] for the LiI 2s-2p transition, is in contradiction to Griem's static treatment of ionic broadening [3]. At this point, it is important to notice, as emphasized in Table 1 of Brissaud et al. [11] (see Eqs. (3.15) and (3.16)), that the definition of the Kubo number K_c depends on the value of Ω/ω_p (ω_p is the plasma frequency, Ω the frequency separation between the upper or lower level of the transition and the main perturbing level). For the isolated lines investigated here, $\Omega/\omega_p > 1$. A simple examination of Griem's criterion (Griem [3], page 94) for the (quasi) static approximation for the ions shows that the left-

* Let us recall that Table 1 of Brissaud et al. [11] and quantities like K_c are only introduced to allow phenomenological discussion and physical understanding but of course are not needed in actual MMM calculations.

Table 2. Comparison between calculated widths and shifts (in Å) at $N = 10^{17}$ cm^{-3} and $T = 2 \cdot 10^4$ K. (1) Griem; (2) MMM; (3) Sahal-Bréchot. For the theory of Griem, total widths and shifts are calculated using the standard formulae (Griem [3], p. 97) with the aid of the ion broadening parameter A, no separate ionic width of shift appearing in the numerical tables.

		Electronic width	Electronic shift	Ionic width (Ar^+)	Ionic shift (Ar^+)	Total width	Total shift
LiI	(1)	0.196	− 0.042			0.199	− 0.045
2s-2p	(2)	0.211	− 0.041	0.012	− 0.020	0.223	− 0.061
	(3)	0.178	− 0.112	0.064	− 0.024	0.242	− 0.136
NaI	(1)	0.212	0.115			0.219	0.123
3s-3p	(2)	0.222	0.095	0.020	0.030	0.242	0.125
KI	(1)	0.555	0.278			0.575	0.301
4s-4p	(2)	0.570	0.238	0.050	0.073	0.620	0.312
CsI	(1)	1.31	0.752			1.39	0.834
6s-6p	(2)	1.26	0.515	0.133	0.169	1.40	0.684
$J = 1/2 - J = 1/2$							
CsI	(1)	1.32	0.824			1.41	0.925
6s-6p	(2)	1.24	0.530	0.141	0.172	1.38	0.702
$J = 1/2 - J = 3/2$							

hand side of his equation 213 can be rewritten in terms of the Kubo number K_c corresponding to the hydrogenic case ($\Omega/\omega_p < 1$)* which is not relevant here. In this hydrogenic case, K_c would be greater than unity which would lead to a static profile of the linear Stark effect type. However, a rough treatment of the ionic broadening can be justified, as long as this broadening is negligible.

Table 2 gives a detailed comparison between the results of Griem [3], of Sahal-Bréchot [4] and of the MMM, for electronic, ionic and total widths and shifts (the MMM Li values have been previously reported by Brissaud et al. [5]). The good agreement — except, surprisingly, for the CsI shift — between the impact calculations of Griem and the MMM calculations for the electronic broadening is noteworthy. The strong disagreement between Sahal-Bréchot and MMM calculations for the ionic width of Li has been previously attributed to the elastic quadrupole contribution, included in the calculations of Sahal-Bréchot and not in the MMM ones. However, taking into account this quadrupolar contribution leads to no appreciable variation of the total width (Table 2) and consequently cannot be checked by the experiment (see Section III).

* More precisely, in the case of quasi-neutrality, the Griem's equations (213)—(214) are equivalent to

$$2.3\,(m_e/m_p)^{1/2}\,(r_0/D)^2\,K_c \gtrsim 1\,,$$

where the frequency Ω does not appear. m_e and m_p are the electronic and the perturber's mass, r_0 and D the mean interparticular distance and the Debye length.

III. Comparison with Experiments

Until recently no measurements of Stark parameters of alkali-metal resonance lines have been published. This lack of experimental data is probably due to the difficulties of observation of pure Stark profiles, i.e. non perturbed by other broadening mechanisms, as resonance or Van der Waals broadening, predominant in usual experimental devices. The self-absorption of resonance radiation has also to be taken into account, in order to obtain reliable data. Very recently Purić et al. [1, 2] have published measurements of Stark widths and shifts of resonance lines of LiI, NaI, KI and RbI. These elements are introduced as impurities in an electromagnetic T-tube driven argon plasma, the electronic density being measured by a single wavelength laser interferometer. The existence of self absorption is checked and found to be negligible. But, on the other hand, the possible influence of other broadening mechanisms is not discussed. In particular, the Doppler width, which still reaches more than 50% of the measured width for Li, is not mentioned.

In Fig. 1, we compare the experimental and the various theoretical results for LiI to RbI, for a temperature range of 10000—40000 K and an electronic density of 10^{17} cm^{-3}. The agreement between experiment and MMM calculations is rather good in the whole range, but some values especially for the shifts are at the limits of the experimental error bars.

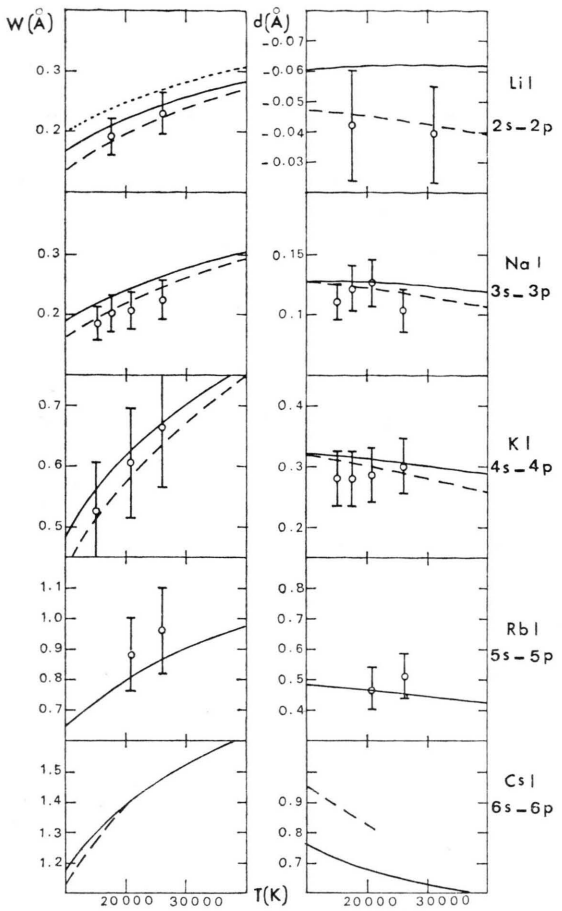

Fig. 1. Total (half) half-widths W and shifts d are shown as functions of temperature T, at $N = 10^{17}$ cm^{-3}. Broken curve, calculations of Griem [3]; dotted curve, calculations of Sahal-Bréchot [4]; full curve, M.M.M. results. The experimental points are those of Purić et al. [2].

Unfortunately, very little information is given on the experimental error causes leading to the indicated uncertainties. From a theoretical point of view, it must be noticed that for this type of line the shift results essentially from a competition between the influence, on the upper level (np), of the lower level (ns) itself and of the two next higher levels (($n+1$)s) and (n'd). (An explicit dependence in terms of line strengths S_i and frequency separations between the levels is given in Section 4.) First, this may give negative shifts as it is the case for the LiI 2s-2p transition for which the contribution of the (2s)-level exceeds the contribution of both the (3s) and (3d)-levels. On the other hand, shifts are obviously very sensitive to the S_i values, a slight variation of S_i leading to crude variations of the resulting shift. For instance a variation of 5% of the line strength corresponding to the two main perturbing levels (s) and (d) yields a variation of 10 to 17% for the total shift (see Table 3). In this connection, it must be emphasized that the corresponding uncertainties given in the tables of Wiese et al. [13] used here as the source of S-values, range from 10% (Li) to 25% (Na and K). For Rb and Cs which do not appear in these tables, we deduce the S-values from the transition probabilities values tabulated by Heavens [14] following the Bates and Damgaard method.

Finally, it has to be mentioned that there is good agreement between theory and experiment, especially for the width, which is dependent on strong fields, although for all the considered elements the values of the ratios r^*/n^2a_0 and r^*/λ are rather small (see Table 1). This confirms the large extent of validity of semi-classical dipolar calculations.

IV. Regularities and Trends

As already pointed out (Wiese [6], Purić et al. [7], Wiese and Konjević [8]), regularities or systematic trends must be expected for Stark parameters of analogous transitions of homologous atoms, due to the atomic quantities involved in the broadening calculations.

This hypothesis has been largely examined by Purić et al. [2], who have found an approximately linear dependence of widths and shifts on the nuclear charge Z, which shows however a noticeable exception for LiI.

Besides the dependence of the profile parameters on Z, Purić et al. expect also a simple relation between widths and shifts expressed in Angströms and the quantity $\lambda^2(n+1)^2$ (λ is the wavelength of the ns-np transition), claiming that the upper

Table 3. Influence of the line strengths uncertainties on the calculated widths and shifts ($N = 10^{17}$ cm^{-3}; $T = 2 \cdot 10^4$ K). (1) results with the values of Wiese et al.; (2) the line strengths of the $np - (n+1)s$ and $np - n'd$ transitions are varied from + 5% for Li and from − 5% for Na and K. The resulting variation is percentage in given in the brackets.

	LiI 2s–2p	NaI 3s–3p	KI 4s–4p
Total width			
(1)	0.223	0.242	0.620
(2)	0.224 (+ 0.4%)	0.235 (− 3%)	0.602 (− 3%)
Total shift			
(1)	−0.061	0.125	0.337
(2)	−0.051 (− 16%)	0.112 (− 10%)	0.279 (− 17%)

level of the line is mainly perturbed by the $(n+1)$s level. But, as aforementioned in Section III, the broadening is the result of the influence of, at least, the two higher levels $(n+1)$s and $(n'$d) and of the lower level $(n$s) of the transition. The role of this last level is far from being negligible and explains for instance the negative shift observed for LiI.

It is thus necessary to look for a dependence of Stark parameters on a more realistic atomic physics factor. In this way, it is interesting to note that a rough analytical estimation of width and shift can be given following the Table 1 of Brissaud et al. [11]. This estimation, based on a simple two-level model leads to width and shift proportional to the quantity $(S_e/\Omega)^{2/3}$, where Ω is the frequency separation between the levels and S_e a corresponding effective line-strength.

Taking into account the existence of several perturbing levels exhibiting rotational degeneracy, and after an angular average over the atom direction, the complete MMM calculation leads to width and shift roughly proportional, for this type of line, to $|x|^{2/3}$ and sign $x \cdot |x|^{2/3}$ respectively, where $x = \sum_i \alpha_i S_i/\Omega_i$. The summation is restricted to the three $(n$s), $((n+1)$s) and $(n'$d) levels, the Ω_i are the (algebraic) frequency separations between these levels and the $(n$p) level, S_i the corresponding actual line strengths, and α_i are angular factors.

In Fig. 2 are plotted theoretical and experimental widths and shifts versus $|x|^{2/3}$ and sign $x \cdot |x|^{2/3}$ respectively. A nearly linear dependence is observed for the resonance transitions through the sequence of the alkalis, including the negative shift of LiI. Obviously, the trends in the S_i and Ω_i values lead to increasing x for increasing atomic number Z. Measurements for Cs would be necessary to confirm both the theoretical results and the phenomenological trend exhibited.

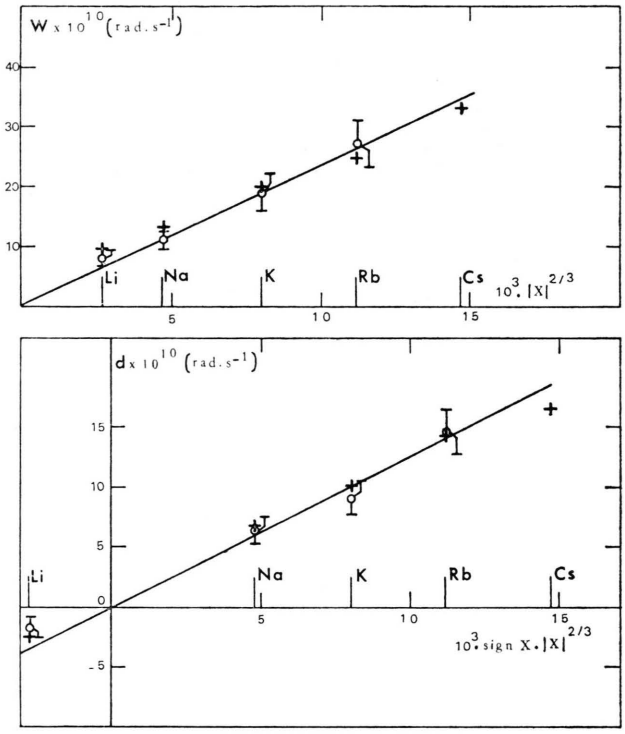

Fig. 2. Experimental (○ Purić et al. [2]) and theoretical (+ M.M.M., $T = 2 \cdot 10^4$ K) widths and shifts plotted as a function of the atomic quantity $|x|^{2/3}$ or sign $x \cdot |x|^{2/3}$ respectively. ($x = \sum \alpha_i S_i/\Omega_i$, S_i expressed in a.u. and Ω_i in cm^{-1}). The straight line is a fit of both experimental and theoretical data.

V. Conclusion

The MMM, which introduces a formalism different from the usual binary collision theory, applied to Stark broadening of alkali metal resonance lines, leads to rather simple, no time-consuming calculations * in agreement with recent experimental results.

This confrontation with experiment confirms also the large validity range of semi-classical calculations, probably due to the statistical character of the radiator perturbation. Further, no evidence has been found that it might be necessary to take into account a quadrupolar contribution to the electronic or to the ionic broadening, as it is done in the numerical tables of Griem [3] (where the smallness of this contribution can be quoted) and in the work of Sahal-Bréchot [4], respectively.

Concerning the question of Stark widths and shifts regularities, the main problem, in order to obtain some reliable predictions, is to introduce appropriate atomic quantities, related to the perturbing levels actually involved in the broadening. Indeed, the broadening of a line does not always depend on the contribution of one level only. It has been shown that such quantities can be found on the basis of the MMM results.

* 0.5 s on the CIRCE I.B.M. 370/168 computer to obtain width and shift for fixed values of N and T.

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