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Influence of inelastic collisions on the width of optical lines involving Rydberg states

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It is shown that with use of some assumptions the cross sections for the broadening of optical lines originating from Rydberg levels can be interpreted with a simple model which takes into account the elastic and the quenching cross sections of the corresponding Rydberg states. The validity of the model is extensively discussed. Good agreement is observed in most cases between the values derived from the model and the available experimental data for the broadening and quenching cross sections of a wide set of Rb and Na Rydberg levels perturbed by noble gases. It is clearly demonstrated that inelastic processes can significantly affect the broadening cross sections even for large values of the principal quantum number n.

I. INTRODUCTION

Experimental studies of Rydberg atom-atom interactions started a half century ago when Amaldi and Segrè[1] measured the shift of spectral lines associated with transitions between the ground-state and highly excited nP states of alkali atoms. Fermi, in a famous paper,[2] laid at the same time the foundations of the theoretical treatment of Rydberg atom-atom interactions. This treatment was based on the fact that the outer electron and the ionic core, being far away from each other on the average, behave as separate scatterers during an atomic collision. Recently, due to the development of new experimental techniques, there has been a strong revival of interest in the physics of Rydberg atoms. Apart from a justifiable curiosity, due to the fact that most of the properties of Rydberg atoms exhibit quite unusual orders of magnitude, more practical reasons also justify the interest of the scientific community because Rydberg states play an important role in laboratory and astrophysical plasmas. Their collisional properties may also affect the overall efficiency of laser isotope separation.

Basically two ways of investigating collisional processes involving Rydberg levels have been used[3]:

(i) Measurements of the inelastic cross sections for the total depopulation (quenching) of a given Rydberg level, which have been widely performed for alkali Rydberg states colliding with noble-gas atoms.

(ii) Measurements of the broadening and shift of spectral lines involving Rydberg levels.

It is a tradition to consider the first type of investigation as belonging to collision physics, and the second to spectroscopy. However, especially for highly excited states, the border between these two fields is not very clear.[3] There exists a wide set of Rydberg levels [Na(nD) and Na(nS) states, Rb(nD) and Rb(nS) states] for which both types of investigations have been performed. It has been already demonstrated[4,5] that, in some cases, inelastic collisional processes can contribute significantly to the broadening of the corresponding Rydberg lines. It seems thus of great interest to investigate under which assumptions a clear theoretical connection between the two types of measurements can be established and to see how the available experimental data compare under these assumptions. This is the main goal of this paper. Finally such a work should also provide valuable tests for the theoretical approaches used for both types of processes (i) and (ii) leading to an overall better understanding of the basic physics of collisional processes involving Rydberg atoms.

The paper will be organized as follows. In Sec. II we recall the basis of the line-shape theories with special attention paid to the validity of the necessary assumptions. It will be shown that, under some assumptions, the broadening cross section corresponds to the sum of elastic and quenching cross sections of the involved Rydberg state. The validity of our simple formula as well as its physical meaning will be extensively discussed. In Sec. III we

summarize the specific theoretical approaches that are used in Sec. IV, devoted to the detailed comparison and discussion between the data available for both types of processes. Some concluding remarks end the paper.

II. THEORETICAL BACKGROUND

In this section we first recall the general equations of the impact line-shape theory. Under proper assumptions that are well fulfilled for Rydberg optical lines, we show that there exists a simple connection between the broadening and collisional cross sections. The contribution of both elastic and inelastic collisional processes on the broadening cross section are then discussed within the frame of a Fermi-type model.[2] Though some expressions concerning the shift of the Rydberg lines are also given, we mainly focus our discussion on the broadening process for reasons that will be briefly mentioned at the end of this section (Sec. II G).

A. Impact approximation for optical lines involving Rydberg states

According to the impact theory, the intensity distribution $I(\omega)$ of the line corresponding to a transition between the initial level α and the final level β is given by the Lorentzian profile

$$I(\omega)=\frac{\gamma_{\alpha\beta}}{2\pi}\frac{1}{(\omega-\omega_0-\Delta_{\alpha\beta})^2+\left[\frac{\gamma_{\alpha\beta}}{2}\right]^2}, \tag{1}$$

where ω_0 is the unperturbed frequency of the $\alpha\rightarrow\beta$ transition. $\gamma_{\alpha\beta}$ and $\Delta_{\alpha\beta}$ denote the half-width and shift of the line, respectively. In the impact approximation, both $\gamma_{\alpha\beta}$ and $\Delta_{\alpha\beta}$ are linearly dependent on the perturber density N and can be written as

$$\gamma_{\alpha\beta}=2N\bar{v}\sigma^{(b)}_{\alpha\beta}, \tag{2}$$

$$\Delta_{\alpha\beta}=N\bar{v}\sigma^{(s)}_{\alpha\beta}, \tag{3}$$

where $\sigma^{(b)}_{\alpha\beta}$ and $\sigma^{(s)}_{\alpha\beta}$ are the effective cross sections[6] for the *impact* broadening and shift of the line, respectively, and $\bar{v}$ is the mean relative velocity of the interacting atoms.

The general nonadiabatic formula for the effective cross sections $\sigma^{(b)}_{\alpha\beta}$ and $\sigma^{(s)}_{\alpha\beta}$ were first derived by Baranger[7] and thoroughly discussed by Sobelman *et al.*[8] It can be written as

$$\sigma^{(b)}_{\alpha\beta}-i\sigma^{(s)}_{\alpha\beta}=\frac{\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)\times\{1-\mathscr{S}^{(l)*}_{\alpha\alpha}\mathscr{S}^{(l)}_{\beta\beta}\}, \tag{4}$$

where k is the wave vector of the perturbing atom. Here $\mathscr{S}^{(l)}_{\alpha\alpha}$ and $\mathscr{S}^{(l)}_{\beta\beta}$ are the diagonal elements of the scattering $\mathscr{S}$ matrix for a particular l value of the angular momentum number for the relative motion of the perturber.

It should be emphasized that the shift and broadening of an *optical* line corresponding to the transition between the Rydberg state α and the low-lying state β (e.g., ground state) is entirely determined by the perturbation of the upper state. Thus it is a very good approximation to ignore the perturbation of the lower state by simply putting $\mathscr{S}^{(l)}_{\beta\beta}=1$ for all l in Eq. (4). In this approximation, which was used in all the theoretical treatments so far proposed, the $\sigma^{(b)}_{\alpha\beta}$ and $\sigma^{(s)}_{\alpha\beta}$ cross sections depend only on the quantum numbers α of the Rydberg level. Then we can ignore the β index and write, according to Eq. (4),

$$\sigma^{(b)}_{\alpha}=\frac{\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)\mathrm{Re}\{1-\mathscr{S}^{(l)}_{\alpha\alpha}\} \tag{5}$$

and

$$\sigma^{(s)}_{\alpha}=\frac{\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)\mathrm{Im}\{\mathscr{S}^{(l)}_{\alpha\alpha}\}. \tag{6}$$

Note finally that the diagonal elements $\mathscr{S}^{(l)}_{\alpha\alpha}$ can always be written as

$$\mathscr{S}^{(l)}_{\alpha\alpha}=\exp(-2\Gamma^{(l)}_{\alpha}-2i\eta^{(l)}_{\alpha}), \tag{7}$$

where $2\eta^{(l)}_{\alpha}$ is the real phase shift and $2\Gamma^{(l)}_{\alpha}$ denotes the total probability of collision-induced transitions from the state α to all other energetically accessible states, for a given l value.

B. Connection between broadening and collisional cross sections

According to the theory of scattering,[8] Eq. (5) can be rewritten as

$$\sigma^{(b)}_{\alpha}=\tfrac{1}{2}Q^{(\mathrm{tot})}_{\alpha}, \tag{8}$$

where $Q^{(\mathrm{tot})}_{\alpha}$ represents the *total* cross section for both elastic and inelastic scattering of the atom in the Rydberg state α on the ground-state perturbing atom. It is generally assumed that $Q^{(\mathrm{tot})}_{\alpha}$ can be expressed in the form

$$Q_\alpha^{(\mathrm{tot})}=Q_\alpha^{(\mathrm{el})}+Q_\alpha^{(\mathrm{inel})} , \tag{9}$$

where

$$Q_\alpha^{(\mathrm{el})}=\frac{\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)\,|\,1-\mathscr{S}_{\alpha\alpha}^{(l)}\,|^2 \tag{10}$$

is the cross section for the elastic scattering and

$$Q_\alpha^{(\mathrm{inel})}=\frac{\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)\{1-|\,\mathscr{S}_{\alpha\alpha}^{(l)}\,|^2\} \tag{11}$$

is the cross section for the inelastic scattering of the atom α on the perturber, i.e., the quenching cross section.

Using Eqs. (8) and (9) one can directly connect the results obtained from pressure-broadening experiments on spectral lines involving Rydberg atoms with those obtained from studies on elastic and inelastic processes. We have to keep in mind that the simple relation given by Eq. (8) is only valid if the perturbation of the lower state can be neglected. This condition is always well satisfied for spectral lines connecting Rydberg levels to the ground state of an atom. If the contribution of the lower state cannot be neglected (for example, in the case of radio-frequency lines between two Rydberg levels), Eq. (4) cannot be significantly simplified.

C. The Fermi-Alekseev-Sobelman model

For sufficiently large values of the principal quantum number n there are, according to Fermi,[3] two factors responsible for the broadening and shift of the spectral lines involving highly excited states. The first factor is the scattering of the atomic electron on the perturbing atom [hereafter referred to as $(e-P)$] and the second factor is the effect of polarization of the perturbing atom due to the ionic core-perturber interaction [hereafter referred to as $(C-P)$]. In the Fermi model these two factors are treated as *statistically independent.*

Applying this model, Alekseev and Sobelman[9] have formulated a more general treatment based on the impact theory. The fundamental assumption in this treatment is that the contribution to the broadening and shift caused by inelastic collisions of Rydberg atoms with the perturbing atoms can be neglected. This corresponds to put $Q_\alpha^{(\mathrm{inel})}=0$ in Eq. (9). It follows that $\Gamma_\alpha^{(l)}=0$ in Eq. (7). Thus $\sigma_\alpha^{(b)}$ and $\sigma_\alpha^{(s)}$ can be expressed [using Eqs. (5)–(7)] in terms of *elastic* scattering phase shifts $\eta_\alpha^{(l)}$.

According to the separation between the $(e-P)$ and $(C-P)$ interactions, one can write [see Eqs. (8) and (9)]

$$\sigma_\alpha^{(b)}=\tfrac{1}{2}(Q_\alpha^{(\mathrm{el})e-P}+Q_\alpha^{(\mathrm{el})C-P}) . \tag{12}$$

The first term accounts for the contribution to the broadening due to the $(e-P)$ interaction. Alekseev and Sobelman[9] derived its explicit expression in terms of phase shifts describing the *elastic* scattering of the quasifree electron on the perturbing atom by combining Eqs. (5) and (7) (with $\Gamma_\alpha^{(l)}=0$) and averaging over the momentum distribution of the Rydberg electron. The second term of Eq. (12) represents the contribution to the broadening due to the $(C-P)$ interaction. Its explicit expression has been derived[9] in the following way. The classical expression of Eq. (5) can be written as

$$\sigma_\alpha^{(b)}\simeq 2\pi\int_0^\infty[1-\cos 2\eta_\alpha(b)]b\,db , \tag{13}$$

where b is the impact parameter and η_α the phase shift due to the total interaction potential V_α as derived from the formula (a straight-line trajectory is assumed)

$$2\eta_\alpha=-\frac{1}{\hbar}\int_{-\infty}^{+\infty}V_\alpha(R(t))dt , \tag{14}$$

where $R(t)$ is the internuclear distance for a trajectory corresponding to a given b value. Alekseev and Sobelman derived the $Q_\alpha^{(\mathrm{el})C-P}$ values [Eq. (12)] by using the polarization potential

$$V_{C-P}(R)=-\frac{\alpha_p e^2}{2R^4} \tag{15}$$

for the evaluation of the phase shifts. In Eq. (15) α_p is the polarizability of the perturbing atom and e the electron charge. The final expression of $Q_\alpha^{(b)C-P}$ as derived from Eqs. (13)–(15) will be recalled in Sec. III.

In a quite similar way Alekseev and Sobelman[9] derived the expression for the contribution of both $(e-P)$ and $(C-P)$ interactions to $\sigma_\alpha^{(s)}$. In the limiting case, when the s wave is only taken into account, i.e., for extremely low electron velocity v_e, the contribution of the $(e-P)$ interaction to the shift can be related directly to the asymptotic value σ_0 of the effective cross section for the elastic scattering of an electron by the perturber for $v_e\to 0$, in the same way as in the original Fermi approach.

Earlier studies on the collisional broadening and shift of the principal series lines ($S-P$ transitions) in an alkali atom perturbed by noble gases[10–12] have shown that, for large n, the purely elastic Alekseev-Sobelman treatment leads to a good agreement with experiment. On the other hand, however, recent experiments or the two-photon ($S-S$)

and $(S-D)$ transitions of Na (Refs. 4 and 5) and Rb (Refs. 13–15) perturbed by noble gases have suggested in some cases the need for the inclusion of inelastic processes in the interpretation of the experimental data.

D. Inelastic collisions

In most theoretical treatments of quenching collisions (i.e., of $Q_\alpha^{(\mathrm{inel})}$) involving highly excited atoms, only the $(e-P)$ interaction is taken into account, the $(C-P)$ interaction being completely neglected.[16–21] This approach leads in general to a reasonable agreement between calculated and measured values for $Q_\alpha^{(\mathrm{inel})}$. Thus, when needed, we will use theoretical approaches taking only into account the $(e-P)$ interaction in order to calculate $Q_\alpha^{(\mathrm{inel})}$. More specific details on some of these approaches will be given in Sec. III.

We should note, however, that the problem of the contribution of the $(C-P)$ interaction to the $Q_\alpha^{(\mathrm{inel})}$ cross sections has become a source of some controversy in the literature.[22–25] Results of coupled-channels calculations recently performed by Hickman[25] indicate that the inelastic cross sections are insensitive to the $(C-P)$ interaction, whereas the elastic cross sections may depend significantly on it.

E. Extended Fermi model

Adapting the Fermi model to the inelastic case, i.e., treating the $(e-P)$ and $(C-P)$ interactions as statistically independent, we can express both $\sigma_\alpha^{(b)}$ and $\sigma_\alpha^{(s)}$ as a sum of two terms due to the $(e-P)$ and $(C-P)$ interactions, respectively. In the general case, the cross sections should be calculated from Eqs. (5) and (6) by computing the diagonal elements $\mathscr{S}_{\alpha\alpha}^{(l)e-P}$ and $\mathscr{S}_{\alpha\alpha}^{(l)C-P}$ of the scattering matrix separately for the $(e-P)$ and $(C-P)$ interactions, respectively. Following Hickman[25] we can neglect the inelastic contribution to the $\mathscr{S}_{\alpha\alpha}^{(l)C-P}$ elements by putting $\Gamma_\alpha^{(l)C-P}=0$ in Eq. (7). This means that the broadening and shift due to the $(C-P)$ interaction will be assumed to be of *purely* elastic nature and thus will be calculated according to the Alekseev-Sobelman treatment.

Combining Eqs. (8), (9), and (12) we finally obtain[26]

$$\sigma_\alpha^{(b)}=\tfrac{1}{2}(Q_\alpha^{(\mathrm{inel})}+Q_\alpha^{(\mathrm{el})e-P}+Q_\alpha^{C-P}) , \tag{16}$$

the two last terms of the right-hand side being the same as in Eq. (12). Equation (16) will be extensively used in Sec. IV.

F. Limitations of the extended Fermi model

It is generally believed that the assumption of statistical independence of the $(e-P)$ and $(C-P)$ interactions, which is the essence of the Fermi model, is well justified for highly excited states, i.e., for large n. For intermediate-n values, i.e., in the region where, as we will see, the maximum of broadening cross sections occur, this assumption may cease to be valid. To our knowledge the only attempt to extend the high-n broadening treatment down into the intermediate region is that given by Omont.[17] To calculate $\sigma_\alpha^{(b)}$, he neglects the inelastic collisions [i.e., $\Gamma_\alpha^{(l)}=0$ in Eq. (7)] and uses the semiclassical Eq. (13), $\eta_\alpha(b)$ being the total phase shifts due to the total interaction potential $V_\alpha(R)$, i.e., including both $(e-P)$ and $(C-P)$ interactions, as calculated from Eq. (14). $V_\alpha(R)$ is taken to be the sum of the polarization potential [Eq. (15)] and the Fermi potential V_F [approximating the $(e-P)$ interaction by a δ function[17]]. In such a way the statistical dependence between the two interactions is approximately taken into account. The final expression of $\sigma_\alpha^{(b)}$ can be written[17] as

$$\sigma_\alpha^{(b)}\approx\tfrac{1}{2}(Q_\alpha^{C-P}+Q_\alpha^{e-P}) , \tag{17}$$

where the first term is the polarization term and the second accounts for the $(e-P)$ interaction.

The numerical value of the first term does not differ significantly from the $Q_\alpha^{(\mathrm{el})C-P}$ value derived by Alekseev and Sobelman.[9] Thus one can conclude (this will be confirmed in Sec. IV) that the Omont result should not differ significantly from what can be expected when the statistical independence between the two interactions is assumed. This is probably due to the rather crude approximations used to derive Eq. (17). Nevertheless it seems that for the intermediate-n region the statistical independence can still be applied. The inaccuracy inherent to this assumption is certainly less than that caused by neglecting the inelastic collisions. Therefore in the present work we assume the validity of the extended Fermi model also for the intermediate-n region, i.e., our analysis of broadening data will be based on Eq. (16). The comparison developed in Sec. IV will allow us to check this assumption.

G. Line-shift cross sections

With the approximations used in the present work only the cross section $\sigma_\alpha^{(s)e-P}$ for the line shift

due to the $(e-P)$ interaction can be affected by inelastic collisions. One can always write this cross section as the sum of the elastic and inelastic contributions. However, there is no direct relationship between $Q_\alpha^{(\mathrm{tot})}$ [Eq. (8)] and the line-shift cross section. No simple formulas analogous to Eqs. (8) and (16) exist for the shift. Therefore in the present work the data concerning the shift of Rydberg lines are not analyzed. We should only mention that the elastic contribution to the shift is identical to that derived by Alekseev and Sobelman[9] and can be expressed in terms of e^--perturber elastic phase shifts.

III. SOME THEORETICAL APPROACHES

We summarize in this section the theoretical approaches that are used in Sec. IV for the detailed comparison, along with some general remarks on their validity.

A. Evaluation of Q_α^{C-P}

We use the Alekseev-Sobelman formula[9]

$$Q_\alpha^{C-P}=2\sigma_\alpha^{(b)C-P}=11.4\left[\frac{\alpha_p e^2}{2\hbar v}\right]^{2/3}, \tag{18}$$

which reduces to

$$Q_\alpha^{C-P}=7.18\left[\frac{\alpha_p}{v}\right]^{2/3}, \tag{18'}$$

in atomic units. This formula was derived using the JWKB phase shifts for the polarization potential [Eq. (15)]. Omont's approach[17] (Sec. II F) leads to a slightly different numerical coefficient [10.1 instead of 11.4 in Eq. (18)] for the polarization contribution to the broadening [first term of Eq. (17)]. Equation (18) has already proved very good agreement with experiment when the two other terms of Eq. (16) are negligible.[10,11] Finally it is important to note that the Q^{C-P} term is n and l independent.

B. Evaluation of $Q_\alpha^{(\mathrm{el})e-P}$

We use the elastic first Born approximation as developed by Hickman[18,19] and by Hugon *et al.*[20] All our computations can be summarized in a simple way for nS and nD states of alkali atoms colliding with noble-gas atoms:

$$Q_{nS}^{(\mathrm{el})e-P}=2.32\times10^8\frac{\mu L^2}{T}n^{*-3.997} \tag{19}$$

and

$$Q_{nD}^{(\mathrm{el})e-P}=5.64\times10^8\frac{\mu L^2}{T}n^{*-4.032}. \tag{20}$$

The cross sections are in $\mathrm{\AA}^2$. μ is the reduced mass of the alkali–rare-gas pair, T the temperature (in K), and L the diffusion length for the elastic e^-–rare-gas scattering in atomic units. n^* is the effective quantum number ($n^*=n-\delta$, where δ is the quantum defect of the considered level). The accuracy of these scaling formulas is better than 2% when compared to the exact computation using the first Born method.[20] Note that we use for the numerical calculations an effective diffusion length, as defined by de Prunelé and Pascale,[27] given by $4\pi L^2=\langle\sigma_e(v_e)\rangle$, where the brackets indicate the average of the elastic cross section σ_e for the e^-–rare-gas scattering over the velocity distribution of the Rydberg electron. The validity of the Born method has already been widely discussed.[19,20,28] We just recall here what seems important for our purpose.[29] The method is only valid for n high enough, say $n\gtrsim10$ in the He case, for which the diffusion length approximation used to derive Eqs. (19) and (20) is clearly valid. For the other rare gases, even if an effective diffusion length is used that takes partly into account the energy variation of σ_e, a lower-n limit for the validity of the method is difficult to define but it is certainly greater than for He. For these reasons we will only quote the results of our model for n values greater than 10.

Omont has also evaluated this term [Eq. (17)]. The numerical results[17] are, in general, close to those obtained by the Born method. Thus for consistency we will restrict our calculations to the method previously described. Note finally that the $Q^{(\mathrm{el})e-P}$ term can be written approximately as $A(l)n^{*-4}$, where $A(l)$ is a weakly l-dependent factor.

C. Evaluation of $Q^{(\mathrm{inel})}$

When available we use the experimental data for $Q^{(\mathrm{inel})}$. Otherwise we use two approaches that take only into account the $(e-P)$ interaction and have already been proven to provide reasonable agreement with the experimental data.[19,20] The $Q^{(\mathrm{inel})}$ term depends on both n and l.

The first one is the inelastic first Born approxi-

mation developed by Hickman.[18,19] The numerical procedure can be found in Hugon *et al.*[29] Its validity has been widely discussed and the same remarks as those quoted in Sec. III B can be repeated here. Finally, as mentioned by Derouard and Lombardi,[29] its use should be limited to processes of small inelasticity ($\Delta E \lesssim 15$ cm^{-1}).

The second theoretical approach is the scaling formula derived by Hickman.[30] It provides a convenient and easy way to evaluate the inelastic processes involving Rydberg atoms. First developed for the angular momentum mixing process,[31,32] it can be extended to other inelastic processes providing its validity requirements are fulfilled. For our purpose it is sufficient to say that it is valid for the Na(nd) states for all rare gases even at low-n values. For the Rb(nS) states it can be used only for n values greater than about 22, 36, 46, 62 for collisions with He, Ne, Ar, and Xe, respectively. For Na(nS) and Rb(nD) levels that are energetically well isolated from the neighboring levels (their quantum defects being about 1.3), the scaling formula cannot be used in the range of n values ($n \lesssim 45$) of interest here.

D. Other theoretical approaches

The model of de Prunelé and Pascale,[27] also based only on the $(e-P)$ interaction, provides a convenient way of directly evaluating the sum $Q_\alpha^{(\mathrm{inel})}+Q_\alpha^{(\mathrm{el})e-P}$. Thus adding the polarization term leads to a quantity that is to be compared to $2\sigma_\alpha^{(b)}$, according to Eq. (16). We refer the reader to the original paper[27] for the detailed expressions derived from this model.

Finally we will also quote $\sigma_\alpha^{(b)}$ theoretical values computed by Wu and Stwalley[33,34] using a classical purely elastic approach identical to Eq. (13). It must be emphasized that this approach is quite different from those developed in this section since the Fermi model is not used, the phase shifts $\eta_\alpha(b)$ being computed using a modified van der Waals long-range potential.

IV. COMPARISON BETWEEN BROADENING AND QUENCHING DATA

All the experimental $\sigma_\alpha^{(b)}$ data exhibit the same n dependence. They first steeply increase with n in a low-n region before they reach a maximum, in what will be called the intermediate-n region, after which a decrease towards an asymptotic limit for higher-n values is observed. The position of the maximum as well as the whole shape of the $\sigma_\alpha^{(b)}(n)$ curve depends strongly, as will be shown, on the relative importance of the three terms of Eq. (16). This section is divided into two parts, one devoted to the discussion of the data concerning the sodium Rydberg states and one devoted to the rubidium Rydberg levels. Before beginning the discussion it is of interest to mention that, for a given perturber, the $Q^{(\mathrm{incl})}$ values strongly depend on the quantum defect δ of the considered levels.[20,31,32] The Na(nS) and Rb(nD) states have a quantum defect of about 1.3 indicating that they are relatively well isolated from the neighboring states in the energy spectrum. In that case, small-$Q^{(\mathrm{incl})}$ values have been measured. The Rb(nS) states ($\delta \sim 3.1$) and Na(nD) states ($\delta \sim 0.02$) exhibit a quantum defect close to an integer value. They are thus energetically close to hydrogenic states of high degeneracy $(n-3)$ F,G,H, etc., levels for Rb(nS) states or n,F,G,H, etc., levels for Na (nD) states. In that case, large-$Q^{(\mathrm{inel})}$ values have been reported. More details on the effect of the energy position of the Rydberg levels on their quenching cross sections can be found in Refs. 3, 19, and 20.

A. Sodium data

The broadening cross sections of $(3S-nS)$ and $(3S-nD)$ lines due to collisions with He, Ne, Ar, Kr, and Xe from $n=5$ to 38 (S states) and $n=4$ to 40 (D states) have been measured using a trilevel echo technique.[4,5] We use all the $\sigma_\alpha^{(b)}$ data published in Ref. 5 for our comparisons. The authors have compared their results with Omont's approach.[17] The $\sigma_{nS}^{(b)}$ cross sections have been shown to agree with the theoretical calculations in the decreasing part of the $\sigma_{nS}^{(b)}(n)$ curve, except for Ne. They have also qualitatively shown that, the $\sigma_{nD}^{(b)}$ cross-section values, which are much larger than the corresponding $\sigma_{nS}^{(b)}$ cross sections, especially in the intermediate-n region, exhibit the clear influence of inelastic collisions.

Measurements of $Q^{(\mathrm{inel})}$ are available for low-nS states ($n \leq 10$) colliding with He, Ar, and Xe,[35] for higher-nS states ($20 \leq n \leq 48$) colliding with Ar (Ref. 36), and for nD states ($n \leq 15$) colliding with He, Ne, and Ar.[31] Using our model we can extend somewhat the analysis of Kachru *et al.*[5] In particular, we will show quantitatively that the inelastic collisions account very well for the difference between the $\sigma_{nS}^{(b)}$ and $\sigma_{nD}^{(b)}$ measured values.

Let us consider the case of the nS states. These

states are nonhydrogenic ($\delta \simeq 1.3$) and thus the corresponding $Q_{nS}^{(\mathrm{inel})}$ values reported are small[35,36] ($\lesssim 100$ Å^2). One can consider that the contribution of inelastic collisions should be negligible for all n values. For example, at $n \sim 30$ in the Ar case,[36] one has $Q_{30S}^{(\mathrm{inel})} \sim 130$ Å^2 to be compared to a polarization-term value of about 2000 Å^2. Only in the xenon case, for which inelastic cross sections can be large at high-n values [Hugon *et al.* for Rb(nS) states[37]], a small contribution to $\sigma_{nS}^{(b)}$ should perhaps be considered. But no measurements are available at high-n values for the Na-Xe pair. We thus neglect the inelastic term of Eq. (16) and compute the two remaining contributions according to Eqs. (18) and (19). The results (that are close to those obtained by Kachru *et al.*[5] following Omont's approach[16]) are in good agreement with the $\sigma_{nS}^{(b)}$ data for all rare gases (except Ne). Typical examples are shown in Fig. 1 for Ar and Kr. Similar agreements are observed for He and Xe.

Note that (as mentioned in Sec. III) the first Born approximation is unable to provide reasonable estimates for the elastic part due to the $(e-P)$ interaction at low-n values.[38] This part contributes significantly to the $\sigma_{(nS)}^{(b)}$ values for n values lower than ~ 14 and ~ 20 for Ar and Kr, respectively. As pointed out by Kachru *et al.*,[5] the case of Ne (Fig. 2) is puzzling. There is a discrepancy of about 1.5 for all n values ($n > 10$). But the measured values are less than the computed ones, which seems surprising since the polarization term [Eq. (18)] should provide a lower limit for $\sigma_{\alpha}^{(b)}$. No explanation (except perhaps a hidden error in the Ne measurements, as suggested by the authors[5]) has up to now been proposed to account for this discrepancy.

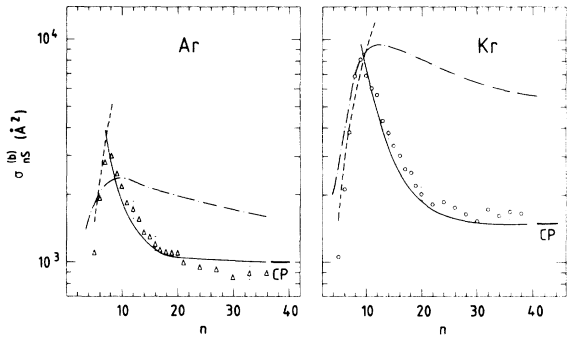

FIG. 1. Broadening cross sections for Na(nS) states perturbed by argon and krypton. (Δ) and (○) are the measurements of Kachru *et al.* (Ref. 5). Some typical error bars are shown. Full line (——) indicates the result of the model computed according to Eq. (16). Dashed line (— — —) shows the theoretical results of Wu and Stwalley (Ref. 34). Dot-dashed line (— · — · —) indicates the result of the de Prunelé-Pascale model (Ref. 27) with addition of the polarization term. This constant term is indicated (CP) on the figure.

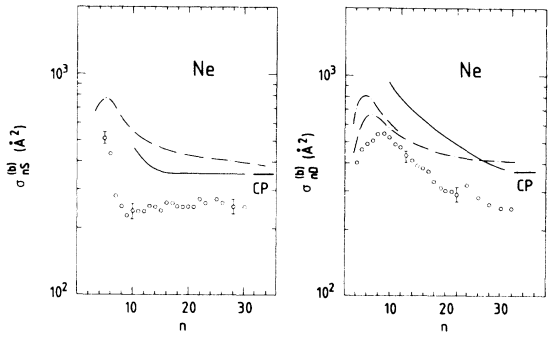

FIG. 2. Broadening cross sections for Na(nS) and Na(nD) states perturbed by Ne. The experimental results are those of Ref. 5. Other notations are the same as in Fig. 1. No results are available from Wu and Stwalley.

Also reported in Fig. 1 are the results of the de Prunelé-Pascale model[27] (with the addition of the polarization term) and the calculation of Wu and Stwalley[33] for low-n values. The de Prunelé—Pascale model exhibits a maximum for the $\sigma_{nS}^{b}(n)$ curve (slightly shifted towards high-n values when compared to the experimental data) but a large discrepancy arises at high-n values, probably indicating that the elastic part due to the $(e-P)$ interaction is noticeably overestimated. The Wu and Stwalley calculations exhibit a satisfactory agreement at low-n values ($n \lesssim 9$) but clearly the extension of this approach to higher-n values will fail, no decrease being expected. However, it shows that a molecular approach is convenient in the low-n range.

The situation appears quite different for the nD states. These states are almost hydrogenic ($\delta \sim 10^{-2}$) and large inelastic cross sections (angular momentum mixing process) have been reported.[31] Kachru *et al.*[5] have shown that the large inelastic cross sections explain the $\sigma_{nD}^{(b)}$ cross-sections values they observed. But their comparison was limited to He, Ne, and Ar for which experimental data up to $n \sim 15$ are available. We extend their comparison to larger-n values and to all perturbing gases by computing $Q_{nD}^{(\mathrm{inel})}$ using the scaling formula of Hickman,[30] the two remaining terms of Eq. (16) being evaluated according to Eqs. (18) and (20). Typical results are shown in Fig. 3 for He and Xe. For $n \geq 12$ (He) and $n \geq 15$ (Xe) the computed values agree within less than 20% with the experimental

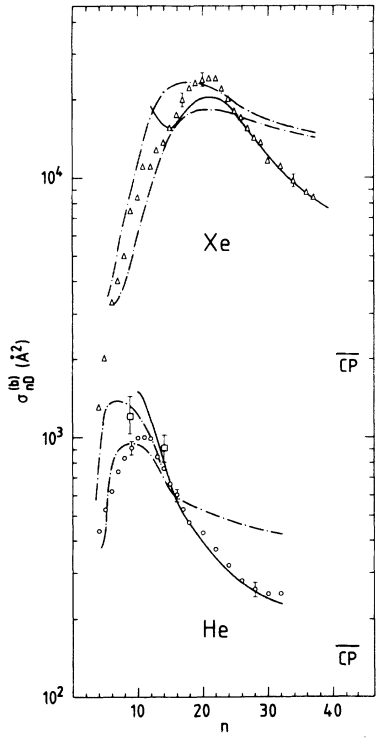

FIG. 3. Broadening cross sections for Na(nD) states perturbed by He and Xe. Experimental results [(○) and (Δ)] are those of Ref. 5. Full line (——) shows the result of the model computed according to Eq. (16). (⊕) are the results of the model when using $Q^{(\text{inel})}$ values reported in Ref. 31 instead of values computed according to the scaling formula of Hickman (Ref. 30). Dot-dashed line (— · — · —) indicates the results of the de Prunelé-Pascale model (Ref. 27) with inclusion of the polarization term. This constant term is indicated (CP) on the figure.

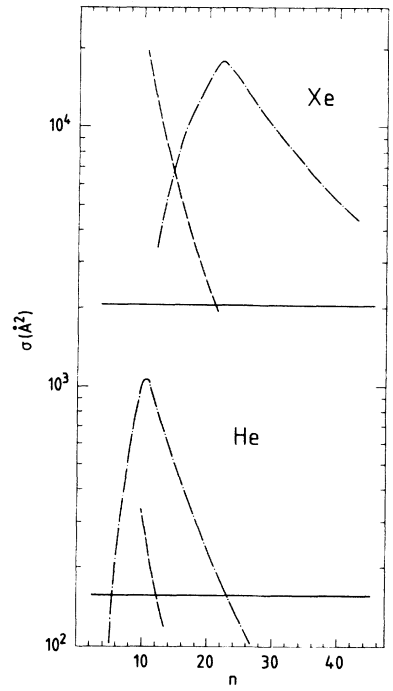

FIG. 4. Relative contributions to the $\sigma^{(b)}$ values of the three terms of Eq. (16) in the case of Na(nD) states perturbed by He and Xe (see Fig. 3). Full line (——) indicates the n-independent polarization term, dashed line (— — —) the elastic part due to the $(e-P)$ interaction, and dot-dashed line (— · — · —) shows the inelastic contribution calculated according to the scaling formula of Hickman (Ref. 30).

data.[39] Much closer agreement is observed in the high-n range. It is not surprising that the agreement observed is better for He than for Xe at lower-n values because $Q_{nD}^{(\text{el})e-P}$ should be more for higher-n values in the Xe case than in the He case as already discussed in Sec. III B. Note, however, that the intermediate as well as the high-n range is well predicted by the simple model in the Xe case, displaying clearly the large inelastic contribution to $\sigma_{nD}^{(b)}$ (Xe). The same is also true for Kr and Ar, for which the same type of agreement for He and Xe is observed, and to a less extent for He because in that case the $Q_{nD}^{(\text{inel})}$ values are smaller than for the heavier rare gases. The relative influence of the three terms of Eq. (16) is displayed in Fig. 4. As mentioned previously, our model cannot be used in the low-n range due to fact that the Born approximation is not valid in that range. The neon case leads to exactly the same remarks for the S states (Fig. 2): the calculated values for $n \gtrsim 10$ are about 1.5 times larger than the measured ones. Finally, as was the case for the S states, the de Prunelé—Pascale model (more precisely its lower limit[27] for the nD states) with addition of the polarization term provides reasonable agreement in the low-n and intermediate-n region, while it noticeably overestimates $\sigma_{nD}^{(b)}$ in the high-n range.

B. Rubidium data

Extensive measurements of $\sigma^{(b)}$, performed by a two-photon Doppler-free technique, are available for Rb(nS) and Rb(nD) states colliding with He, Ar ($7 \leq n \leq 35$) and Xe ($7 \leq n \leq 60$). This set of data[14,15] serves as a basis for comparisons. Other $\sigma^{(b)}$ data are also available for some Rb(nS) and Rb(nD) states ($n \sim 25$) colliding with rare gases.[13] Measurements of $Q_{\alpha}^{(\text{inel})}$ have been performed by

Hugon *et al.*[20] for nS and nD states colliding with He for intermediate-n values ($9 \leq n \leq 18$). One value is also available for the 16 S level colliding with Xe.[20] More recently these measurements have been extended to the high-n region ($32 \leq n \leq 45$) for nS states colliding with He, Ne, Ar, and Xe and for nD states in collisions with He and Xe.[37]

For our comparison we mainly use the experimental $Q_{\alpha}^{(\text{inel})}$ values. We recall that the scaling formula of Hickman[30] cannot be applied in most cases (see Sec. III). We quote also the results of Omont's approach.[17]

Let us begin with the nD states. The measured $Q_{nD}^{(\text{inel})}$ cross-section values are always smaller than the corresponding $Q_{nS}^{(\text{inel})}$ values, due to the fact that the nS states ($\delta \simeq 3.1$) are energetically close to the $(n-3)F,G,H$, etc., levels. Figure 5 shows the data for He and Xe. The model provides good agreement in the He case in the intermediate-n range. It is interesting to note that in this range the three terms of Eq. (16) contribute significantly to the broadening cross section, as shown in Fig. 6 where the inelastic part has been computed for $n \lesssim 20$ according to the first Born method.[40] In the high-n range, a small contribution of the inelastic collisions is also present, and the results of the model (experimental $Q^{(\text{inel})}$ values from Hugon *et al.* are used[20,37]) are lying slightly above the asymptotic value, due to the polarization term, computed according to Eq. (18). The effect of the inelastic collisions is, as expected, even more clear in the xenon case. At high-n values ($n \sim 40-50$) the broadening cross sections are significantly larger at the polarization limit. The results of the model, using the experimental $Q^{(\text{inel})}$ values given by Hugon *et al.*[37] are in good agreement with the measurements of Refs. 14 and 15. For both He and Xe the purely elastic approach of Omont[17] leads to underestimated values. The de Prunelé and Pascale model[27] (with addition of the polarization term) exhibits overestimated values for $n \gtrsim 10$ (the results are not shown in the figure) as was the case for the Na Rydberg levels.

A clear effect of inelastic collisions appears also for nS states (Fig. 7). It is, as expected, even greater than for the nD states. This can be inferred from the fact that, for corresponding levels, the difference between the measured $\sigma^{(b)}$ values and the values deduced from the purely elastic model of Omont are larger than for the nD states. This is not surprising in view of the fact that the nS states are, as mentioned above, energetically close to the $(n-3)$ F,G,H, etc., levels. In the He case, for intermediate-n values, the results of the model, using the experimental $Q^{(\text{inel})}$ values of Hugon *et al.*,[20,37,41] agree well with the experimental $\sigma^{(b)}$ values[14,15] (we do not quote in Fig. 7 the $\sigma^{(b)}$ values of Ref. 13 since they agree satisfactory well with the more extensive data of Weber and Niemax[15]). For the highest-n values the influence of inelastic collisions, though small, appears not negligible. The conclusions of the comparison are basically the same for the Xe case. The only $Q^{(\text{inel})}$ value avail-

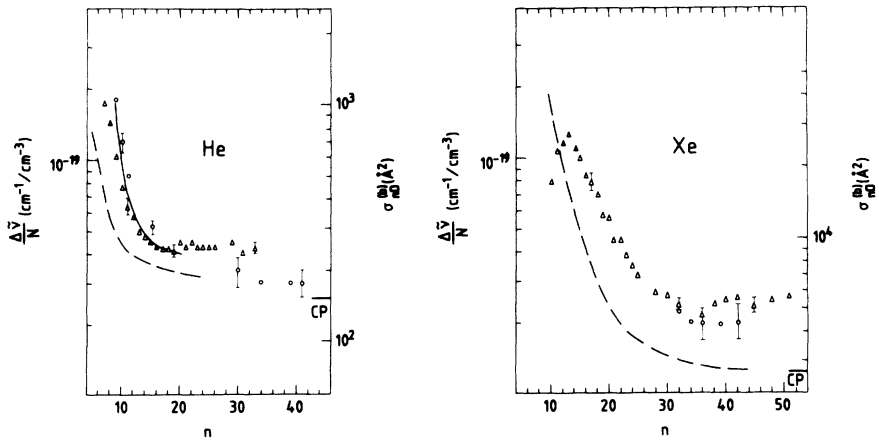

FIG. 5. Broadening rate constants (left scale) and cross sections (right scale) for Rb(nD) states perturbed by He and Xe. The experimental results of Weber and Niemax (Refs. 14 and 15) (with some typical error bars) are indicated by the triangles (Δ). Full line (——) shows the result of the model (in the helium case) computed according to Eq. (16). First Born approximation is used to evaluate $Q^{(\text{inel})}$. Circles (○) are derived from the same Eq. (16) when measured $Q^{(\text{inel})}$ values from Ref. 37 are used. Dashed line (— — —) indicates the result of the purely elastic approach of Omont (Ref. 17). Also shown is the constant polarization term (CP).

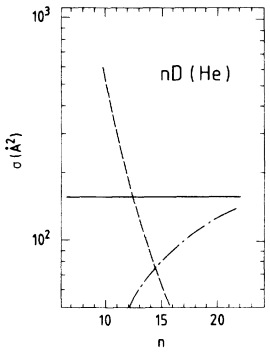

FIG. 6. Relative contribution to the $\sigma^{(b)}$ values of the three terms of Eq. (16) in the case of Rb(nD) states perturbed by He (see Fig. 5). Full line (——) indicates the polarization term, dashed line (— — —) the elastic part due to the $(e-P)$ interaction and dot-dashed line (—·—·—·) shows the inelastic contribution calculated according to the first Born approximation.

able in the intermediate-n range ($n=16$) leads to a computed $\sigma^{(b)}$ value, according to our model, in close agreement with the one measured by Weber and Niemax.[15] At high-n values ($n\sim 40-45$), the results of the model agree well with the measured $\sigma^{(b)}$ values and display a clear influence of the inelastic collisions. For $n\sim 45$ the inelastic contribution to $\sigma^{(b)}$ is about 1.5 times the polarization term [the elastic part due to the $(e-P)$ interaction being almost negligible]. Once again the de Prunelé—Pascale model,[27] with addition of the polarization term, noticeably overestimates the $\sigma^{(b)}$ values for $n \gtrsim 10$ (results are not shown in Fig. 7).

Unfortunately no measurements of $\sigma^{(b)}$ have been performed for Rb Rydberg states colliding with neon. They should be of great interest in order to see if the situation observed for the Rydberg Na states still occurs, i.e., if the $\sigma^{(b)}$ values are noticeably smaller than the theoretical high-n limit provided by the polarization term. Note, however, that, for Ne, the contribution of the inelastic collision to $\sigma^{(b)}$ should be negligible (as was the case for Na Rydberg levels) in view of the small-$Q^{(\mathrm{inel})}$ values reported by Hugon *et al.*[37]

V. CONCLUDING REMARKS

We have shown that, if, according to Fermi, the statistical independence between the $(e-P)$ and $(C-P)$ interactions is assumed, there exists a simple relation between the broadening and the quenching cross sections (this holds only if, as is always assumed, the influence of the lower state of the Rydberg optical line is neglected). This relation provides a useful connection between two different types of measurement, i.e., the line-profile studies and the experiments on collisional inelastic processes. This extended Fermi-type model has been tested in various situations for which the three contributions to $\sigma^{(b)}$ [Eq. (16)] have been observed to be of different relative magnitude, and has been proved to provide good agreement, except in the Ne case, with the measured $\sigma^{(b)}$ cross-section values in both intermediate- and high-n regions. The low-n region clearly requires a more elaborate treatment. In this region the Wu and Stwalley approach as well as the

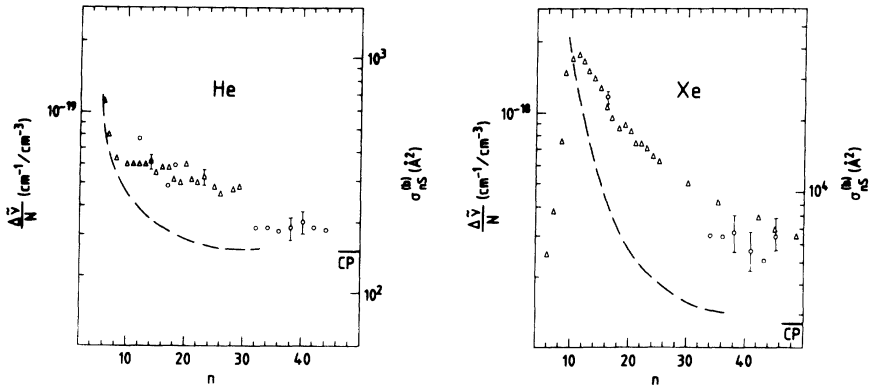

FIG. 7. Broadening rate constants (left scale) and cross sections (right scale) for Rb(nS) states perturbed by He and Xe. The experimental results of Weber and Niemax (Refs. 14 and 15) (with some typical error bars) are indicated by the triangles (Δ). Circles (○) show the result of the model computed according to Eq. (16), the $Q^{(\mathrm{inel})}$ values being those reported in Refs. 20, 37, and 41. Dashed line indicates the result of the purely elastic approach of Omont (Ref. 17). Also shown is the constant polarization term (CP).

de Prunelé–Pascale model show qualitative agreement with the experimental data. Finally the agreement observed between the measured and calculated $\sigma^{(b)}$ cross-section values indicate that in the intermediate-n region the possible interference effects due to the breakdown of the hypothesis of statistical independence between the $(e-P)$ and $(C-P)$ interaction should be small.

It is believed that the extended Fermi model should allow one to obtain quantitative informations on collisional inelastic processes from line-broadening measurements and vice versa. This somewhat erases the traditional border between the two fields.

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[39]The use of the measured $Q_{nD}^{(\text{inel})}$ values (Ref. 31) does not modify conclusions since they are in fairly good agreement with the Hickman's scaling formula (see Fig. 3).
[40]In the rubidium case we use mainly experimental $Q^{(\text{inel})}$ values to evaluate $\sigma^{(b)}$ according to Eq. (16). Hugon *et al.* (Ref. 37) have also performed some calculations of $Q^{(\text{inel})}$ using the first Born approach even for high-n values ($n \sim 30$). Since these calculations are in satisfactory agreement with the experimental values (Ref. 37), they do not modify our conclusion.
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