PRESSURE EFFECTS ON SPECTRAL LINES*

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Intensity distribution, width and shift of pressure broadened spectral lines as well as profiles of satellite bands accompanying these lines are discussed. Results of recent calculations are reviewed and compared with experiment. Problems regarding specific broadening effects (pressure induced transitions, correlations between Doppler and collision broadening) are also indicated.

1. Introduction

The influence of pressure on the shape, width and position of spectral lines has been known for a long time [1–4]. This report intends to emphasize that area of work on pressure broadening phenomena done during the last few years which has seen numerous theoretical efforts together with extensive experimental investigations examining and stimulating theoretical results. I wish to draw particular attention to one important aspect of pressure broadening, namely this connected with its applications in studies of interatomic interactions [3–6]. It has long been recognized that the profiles of pressure broadened spectral lines reflect the interaction potentials of the colliding particles for the initial and final state of the radiating atom. Whereas, information about interactions between atoms in the ground state is available from atomic beam experiments, the line-shape measurements can provide information about interactions involving excited levels.

The phenomenon of pressure broadening has been theoretically investigated using a variety of both classical and quantum-mechanical methods. Most of the theoretical studies have considered either the limit of a low-pressure and high-temperature gas ("impact theory") or a dense low-temperature gas ("quasistatic theory") [1–3]. The impact theory giving a Lorentzian shape with both the half-width and shift proportional to the density of perturbers is usually valid in the core of the line. On the other hand, the quasistatic theory yields a good approximation to the profile of far wings of the line [5, 6].

In most works, so far performed, the parameters describing the interaction potentials have been determined from measurements of the half-width and shift of the line using the impact theory. Such a procedure is analogous to that based on the measurements of total

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cross sections in molecular beam experiments. However, as Behmenburg [5] and Gallagher et al. [6] have pointed out, much more information on interatomic potentials may be derived from the intensity distribution (i.e. differential cross sections) in the line, especially in far wings, where the quasistatic theory holds.

In the intermediate frequency range (i.e. the region between the impact core and quasistatic wing) both limiting theories fail.

We will discuss here some results of recent work on line profiles in far wings and intermediate frequency range as well as in the core of the line. First of all we will focus our attention on the unified treatment of pressure broadening developed recently [7] which permits calculations of the intensity distribution also in the intermediate frequency range. This treatment is based on the quasimolecular formulation of line broadening theory proposed many years ago by Jabłoński [8–10]. In 1931 Jabłoński [8] first recognized the analogy between the mechanism of pressure broadening and of the production of molecular spectra. Starting from this analogy the line shape can be calculated assuming the Born-Oppenheimer approximation and the Franck-Condon principle (FCP) [9, 10]. Such an approach, which was further developed by Baranger [11, 12] and others [13–15] is adiabatic in nature because it neglects the transitions between different levels of the radiating atom induced by the inelastic collisions with perturbing atoms. Non-adiabatic effects which are thus ignored may be very important near line centre [12], but for the intermediate frequency range and for the wings these effects can be nearly always neglected.

2. Unified Franck-Condon line shape

In the quasi-molecular theory [7–15] the system of radiating atom plus perturber-bath is treated as a huge molecule. The shape of the broadened line is then determined in the way analogous to that for the intensity distribution in molecular continuum radiation, i.e. by the calculation of Franck-Condon overlap integrals for free-free transitions.

Let $|i\rangle$ and $|f\rangle$ denote the total wavefunctions of the system composed of one radiating atom and n perturbers for the initial and final level of the radiating atom, respectively. In the Born-Oppenheimer approximation both $|i\rangle$ and $|f\rangle$ can be written as the products:

$$|i\rangle = |\varphi_i\rangle\,|\Psi_i^{(n)}\rangle, \qquad |f\rangle = |\varphi_f\rangle\,|\Psi_f^{(n)}\rangle, \tag{1}$$

where $|\varphi_i\rangle$ and $|\varphi_f\rangle$ denote the electronic wavefunction of the radiating atom, which depend parametrically on the coordinates of perturbers. The wavefunctions $|\Psi_i^{(n)}\rangle$ and $|\Psi_f^{(n)}\rangle$ describe the translational motion of n perturbers for the initial and final level of the radiating atom, respectively.

Using Eq. (1) and applying what is called the Condon approximation (or the quantum-mechanical form of FCP) we may express the electric dipole transition moment $\langle i|\boldsymbol{\mu}|f\rangle$ as

$$\langle i|\boldsymbol{\mu}|f\rangle \simeq \boldsymbol{\mu}_{if}^{(0)}\langle\Psi_i^{(n)}|\Psi_f^{(n)}\rangle, \tag{2}$$

where

$$\boldsymbol{\mu}_{if}^{(0)} = \langle\varphi_i|\boldsymbol{\mu}|\varphi_f\rangle \tag{3}$$

is the radiating dipole moment assumed to be independent of perturbers positions.

The theoretical treatment is greatly simplified if we can neglect the interactions between perturbers. In such a case the wavefunction $|\Psi_i^{(n)}\rangle$ (or $|\Psi_f^{(n)}\rangle$) can be written as a product of one-perturber wavefunctions $|\Psi_i^{(1)}\rangle$ (or $|\Psi_f^{(1)}\rangle$). Using this model one can derive a "unified Franck-Condon" (UFC) expression for the intensity distribution $I(\omega)$ in the broadened line as was done in the recent paper of Baylis and the present author [7]. The UFC line shape is given by

$$I(\omega) = \frac{1}{\pi} \frac{F(x)}{x^2 + \left(\frac{\gamma}{2}\right)^2}, \tag{4}$$

where $x = \omega - \omega_0 - \Delta$, ω_0 denotes the unperturbed frequency of the line. Here γ and Δ are given by the formula

$$\frac{\gamma}{2} + i\Delta = \frac{\pi N \hbar}{\mu} \left\langle \frac{1}{k_i} \sum_{l=0}^{\infty} (2l+1) \{1 - \exp[2i(\delta_l' - \delta_l'')]\} \right\rangle, \tag{5}$$

where the summation is over the quantum numbers l of the angular momentum of the relative motion and the symbol $\langle \ldots \rangle$ indicates the average over initial wave vectors k_i of the perturber (or the initial energies $\varepsilon_i = \frac{\hbar^2 k_i^2}{2\mu}$ with μ — the reduced mass of the radiating and perturbing atoms).

In Eq. (5) δ_l' (or δ_l'') is the scattering phase shift for the upper (or lower) level of the radiator and N is the density number of perturbers. In Eq. (4) $F(x)$ is essentially a sum of reduced free-free Franck-Condon factors $H_l(x)$ (cf. [7]):

$$F(x) = \left\langle \frac{\pi \hbar}{2\mu k_i} \sum_{l=0}^{\infty} (2l+1) |H_l(x)|^2 \right\rangle. \tag{6}$$

To determine $H_l(x)$ the one-perturber radial wavefunctions $\psi_l'(r)$ and $\psi_l''(r)$ for the upper and lower state of the radiator, respectively, must be found (r — the distance between the radiating and perturbing atoms). In the JWKB approximation $H_l(x)$ is given by [7]

$$H_l(x) = \frac{2\mu x}{\hbar} \int_{r_t}^{\infty} \frac{\cos \Phi_l(r)}{k_l(r)} dr \tag{7}$$

with

$$k_l(r) = \left\{ \frac{2\mu}{\hbar^2} [\varepsilon_i - V_i(r)] - \frac{l(l+1)}{r^2} \right\}^{1/2} \tag{8}$$

and

$$\Phi_l(r) = \frac{\mu}{\hbar^2} \int_{r}^{r} \frac{\hbar x - \Delta V(r)}{k_l(r)} dr. \tag{9}$$

Here $V_i(r)$ is the interaction potential for the initial level of the radiating atom and $\Delta V(r) = V'(r) - V''(r)$, where $V'(r)$ (or $V''(r)$) denotes the interaction potential for the upper (or lower) level of the radiator, respectively. In Eqs. (7)—(9) r_t denotes the classical turning point.

Eq. (4) with $H_l(x)$ given by Eq. (7) was shown [7] to be unified in the sense that it yields the Lorentzian shape in the core of the line and the quasistatic shape for the extreme wing and permits calculation of the shape in the intermediate frequency range.

3. *Line wings*

In order to determine the line profile in the wings we need $H_l(x)$ at large x. At large x the main contribution to $H_l(x)$ (Eq. (7)) comes from the regions of stationary phase, i.e. from the vicinity of "Condon points" r_c at which $\left(\frac{d\Phi_l(r)}{dr}\right)_{r_c} = 0$. According to Eq. (9) this condition is equivalent to

$$\hbar x = \Delta V(r_c). \tag{10}$$

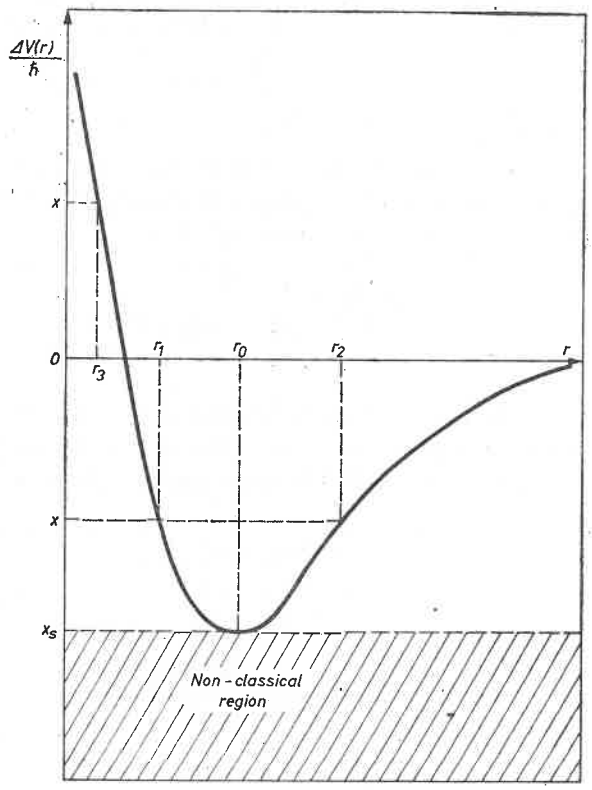

Fig. 1. Typical view of the dependence of potential difference $\Delta V(r)$ on interatomic separation r. r_1, r_2 and r_3 — real Condon points for $x \geqslant x_s$

Thus solving this equation we can express the distance r between interacting atoms by means of the frequencey displacement x. We have to bear in mind, however, that generally r may be a multivalued function of x. The typical view of the dependence of $\Delta V(r)$ on r is shown in Fig. 1, where r_0 denotes the distance of the minimum of $\Delta V(r)$. Denoting by x_s the value $x_s = \frac{1}{\hbar}\Delta V(r_0)$ we can see that for $x \geqslant x_s$ there are real solutions r_c of Eq. (10). For $0 > x \geqslant x_s$ there are two real Condon points r_1 and r_2, which tend to coalesce when x approaches x_s. When $x < x_s$ there are no real solutions of Eq. (10) and we are dealing with complex Condon points r_c.

Using the uniform approximation to evaluation of integral in Eq. (7) we were able to obtain the following formula for the UFC profile in the line wings [7]:

$$I(\omega) = \frac{24\pi N\hbar x^2}{x^2 + \left(\frac{\gamma}{2}\right)^2} \sum_c \frac{|\pi z_c|^{1/2} r_c^2 L(z_c)}{\left|\frac{d\Delta V(r)}{dr}\right|_{r_c}} \exp\left(-\frac{V_i(r_c)}{kT}\right), \tag{11}$$

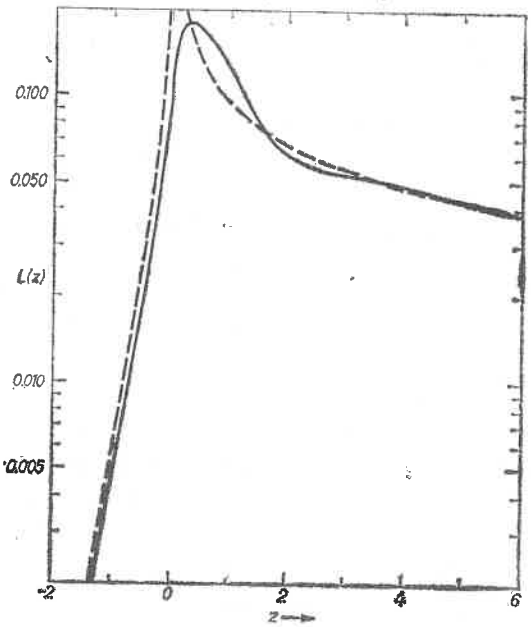

Fig. 2. Universal line shape function $L(z)$ (full line). Dashed lines: asymptotic behaviour for $z > 0$: $L(z) \approx (36\pi z)^{-1/2}$ (quasistatic limit) and for $z < 0$: $L(z) \approx (108\pi|z|)^{-1/2} \exp(-12^{1/3}|z|)$ (antistatic limit)

where z_c is the reduced frequency:

$$z_c = \tfrac{1}{2}\left(\frac{\mu}{kT}\right)^{1/3} \left(\frac{1}{\hbar}\frac{d\Delta V(r)}{dr}\right)_{r_c}^2 \left|\frac{1}{\hbar}\frac{d^2\Delta V(r)}{dr^2}\right|_{r_c}^{-4/3}, \tag{12}$$

and $L(z_c)$ is the universal line shape function

$$L(z_c) = \int_0^\infty d\zeta \zeta^{-2} |\mathrm{Ai}(-z_c\zeta)|^2 \exp(-\zeta^{-3}), \tag{13}$$

where Ai(x) denotes the Airy function. The function $L(z_c)$, which is identical with the function $T(-z_c, \infty)$ introduced by Sando and Wormhoudt [15] is tabulated in Ref. [7] and its plot on z_c is shown in Fig. 2.

A. Quasistatic limit

For $x \geqslant x_s$, i.e. for real Condon points, the line shape in Eq. (11) is determined by the function $L(z_c)$ with positive z_c. If the Condon points r_1 and r_2 (Fig. 1) are well separated then z_c is large. Using the asymptotic form of $L(z_c)$ for $z_c \gg 1$ one can show [7] that for $|x| \gg \gamma$ Eq. (11) reduces to

$$I(\omega) \simeq 4\pi N\hbar \sum_c \frac{r_c^2 \exp\left(-\frac{V_i(r_c)}{kT}\right)}{\left|\frac{d\Delta V(r)}{dr}\right|_{r_c}}. \tag{14}$$

This is the well known one-perturber quasistatic profile [1–3], which is obviously singular for $r_c = r_0$, i.e. for the extrema of $\Delta V(r)$.

For more than forty years there have been reports of diffuse intensity maxima, usually called the satellite bands, occurring in the wings of pressure broadened atomic spectral lines [1–3]. The origin of these bands has been a source of controversy for a long time. Recent careful measurements made at low perturber densities [6, 16–20] together with several calculations [7, 15, 18] appear to corroborate the quasistatic explanation [2]. According to this the primary mechanism in the formation of satellites is the enhancement of the spectral distribution in regions where potential curves in the upper and lower state run parallel, i.e. where the forces in both states are equal and the one-perturber profile (Eq. (14)) is singular. Hindmarsh and Farr [2] have shown, however, that problems with such singularities may be avoided if the multiple interactions with perturbers are taken into account. Using this version of quasistatic theory McCartan and Hindmarsh [17] were able to get a good agreement of the calculated profile of the red satellite accompanying the 4047 Å line of potassium perturbed by Kr with the experimental one.

I would like to emphasize that the UFC line shape (Eq. (11)) has no singularities at all as one follows directly from properties of the universal function $L(z_c)$ (Fig. 2). The maximum of $L(z_c)$ does not occur at the classical satellite position $z_c = 0$, but rather at $z_{max} = 0.3288$. Thus from the point of view of the UFC theory the position of the maximum of the satellite band is not identical with the "classical satellite frequency" x_s as was assumed in previous analyses based on the Hindmarsh-Farr theory.

B. Antistatic limit

The classically inaccessible region of frequencies $x < x_s$ in the spectral line corresponds to the complex Condon points (Fig. 1). The complex Condon points can give, however, the real contributions to the intensity distribution, which as was shown [7, 15] characteristically falls off exponentially with increasing separation from the classical satellite frequency x_s. This exponential profile (called the "antistatic" one in Ref. [7]) has the same form as the

quasistatic distribution in Eq. (14) but is smaller by a factor $3^{-1/2}\exp(-12^{1/3}|z_c|)$. The antistatic profile is mainly responsible for the shape of the long-wavelength side of the red satellite band. Let us mention further that the measurements of positions of maxima of satellites as well as the intensity distribution in the antistatic part of the spectral line may also serve as a source of information about the interatomic potentials.

C. The UFC satellite bands

The calculation of line shape from the UFC formula in Eq. (11) requires the knowledge of $\Delta V(r)$ and its first and second derivatives. Assuming $\Delta V(r)$ in the form of a Lennard-Jones (LJ) potential I have completed recently calculations for the long-wavelength wings of the 4593 and 3889 Å lines of Cs perturbed by Xe. Results of these calculations are

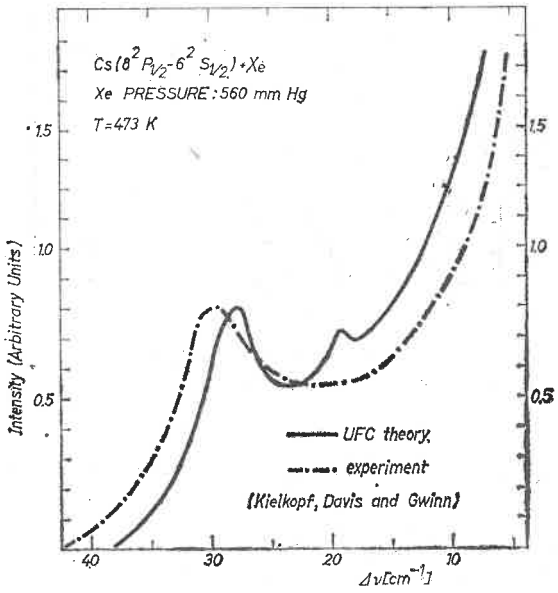

Fig. 3. Comparison of the UFC shape of satellite band at Cs-3889 Å line broadened by Xe (full line) with experimental shape [18a] (dashed line). Calculated shape corresponds to $\varepsilon = 29.1$ cm^{-1} and $r_0 = 11.1$ Å

shown in Figs. 3 and 4, where they are compared with the experimental data of Kielkopf et al. [18a]. The van der Waals constants C_6 used in these calculations were taken from the paper of Mahan [22]. The repulsive constants C_{12} in LJ potentials, which may be expressed by means of C_6 and the depth ε of $\Delta V(r)$ cannot be calculated theoretically. Therefore, in the present calculations ε were treated as empirical parameters. Curve *1* in Fig. 3 and the continuous line in Fig. 4 represent the UFC shape for $\varepsilon = -\hbar x_m$, where x_m is the measured position of the maxima of red satellites found in Ref. [18a]. Let us note that in the Hindmarsh-Farr theory $x_m = x_s$. However, this is not the case in the UFC theory, namely the UFC maxima of red satellites are situated closer to the main line than those of the Hindmarsh-Farr theory.

The influence of ε on the UFC profile of satellites is illustrated in Fig. 4, where the curve *2* corresponds to the value 15% greater than the "Hindmarsh value" $\varepsilon = -\hbar x_s$.

As can be seen from Figs. 3 and 4 the UFC theory yields profiles which are in a reasonable agreement with experiment. However, additional calculations with more realistic

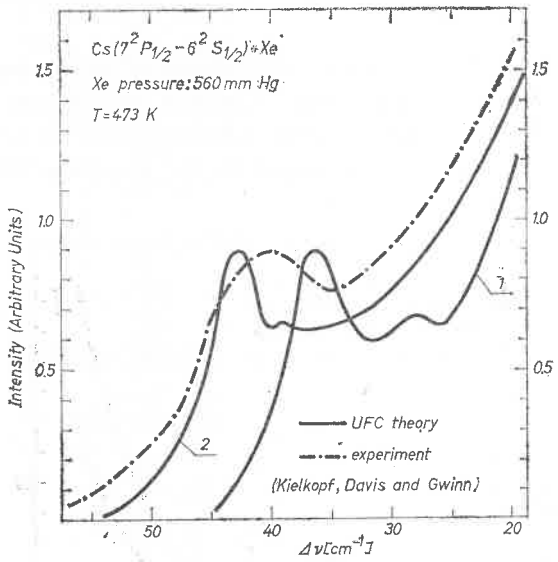

Fig. 4. Comparison of the UFC shape of satellite band at Cs-4593 Å line broadened by Xe with experimental shape [18a] (dashed line). Curve *1*: UFC for $\varepsilon = 39.2$ cm^{-1}, $r_0 = 8.71$ Å; Curve *2*: UFC for $\varepsilon = 45.1$ cm^{-1}, $r_0 = 8.49$ Å

potentials such as those given first by Baylis [23] and then by Pascale and Vandeplanque [24] are necessary.

Using the measured positions of maxima of red satellites at Cs principal series Kielkopf [25] was able to estimate potential curves for several excited states of Cs.

Let us mention further that there is an analogy between the appearance of red satellites and the "rainbow effect" in molecular beam scattering [26].

D. Interaction potentials from line wings data

Gallagher et al. [6] at JILA in Boulder, Colorado have developed an inversion technique which enables one to determine the interaction potential from the shape of extreme wings without assumption of any particular form of $\Delta V(r)$. This technique is based on the quasistatic distribution given by Eq. (14). For small interatomic distances the Boltzmann factor plays usually an important role and this is a cause of the temperature dependence of the shape of line wings. An example of the temperature dependence found in emission by Gallagher et al. [6b] for the Rb-7800 Å line broadened by Kr is shown in Fig. 5. Let us note that opposite temperature dependences are observed on the red and blue sides of the line. From the temperature dependence of the intensity at different frequencies x

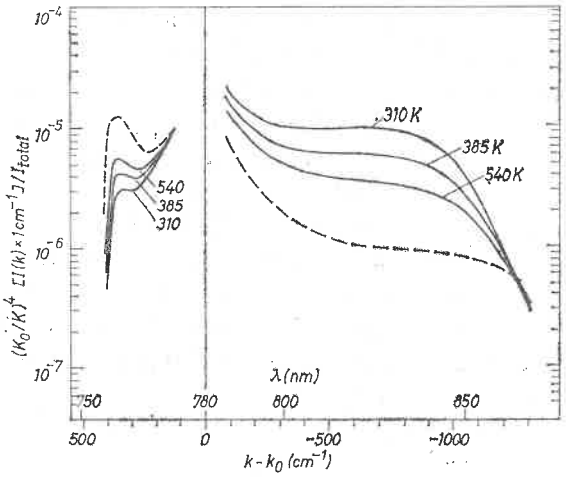

Fig. 5. Normalized emission spectrum of the Rb-7800 Å line broadened by Kr at $N = 10^{19}$ cm^{-3}. The gas temperature are indicated (from Ref. [6b])

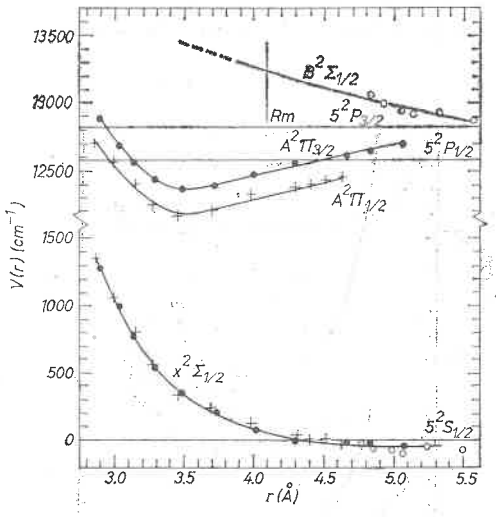

Fig. 6. The Rb-Kr interaction potentials inferred from the data in Fig. 5 (from Ref. [6b])

one can determine both $V'(r)$ and $V''(r)$. The resulting potentials obtained in Ref. [6b] for Rb + Kr are shown in Fig. 6.

Using the measurements of temperature or pressure dependence of the profile in line wings Gallagher et al. [6] were able to construct potential curves for different alkali atoms interacting with noble-gas atoms. Similar studies have been done by Behmenburg et al. [5] in Düsseldorf for mercury vapours mixed with noble gases.

Quite recently Cheron, Scheps and Gallagher [77] have reported results of their emission measurements of the shapes of the thallium 5350 and 3776 Å resonance lines broadened by noble gases. They have studied the Lorentzian-shaped line cores as well as

the transitions to non-Lorentzian regions, satellites bands and profiles in the wings. The comparison of their measurements with the UFC theory the Van der Waals potentials shows qualitative but not quantitative agreement (see Fig. 9 of Ref. [77]). This can be attributed primarily to the fact that the actual long-range interaction between Tl and noble-gas atoms appears to vary somewhat more slowly than r^{-6}.

Another aspect of profiles in line wings, namely that connected with the self broadening, has been studied by Niemax and Pichler [27] in Kiel, who found asymmetries for self-broadening alkali resonance lines. Awan and Lewis [21] in Newcastle have recently reported results of their absorption measurements of the selfbroadened Rb resonance lines. They found satellites in the inner wing region of each resonance line of Rb and showed that these satellites were considerable fainter than the features frequently observed due to perturbation by noble gases.

E. Pressure induced transitions

In 1975 Happer et al. [75] at Columbia University in New York have discovered strong visible emission bands from Cs — noble-gas and Rb — noble-gas systems (at noble gas pressures of a few atmospheres) excited with blue lines of an argon-ion laser. The dominant features of the spectrum are the yellow bands, whose maxima shift system-

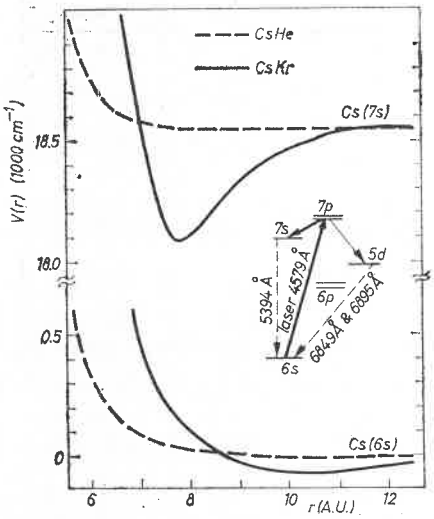

Fig. 7. Potential curves for Cs-Kr and Cs-He according to Pascale and Vandeplanque [24] and scheme of excitation of yellow emission bands in experiments of Tam et al. [75a]

atically toward the red for the heavier noble gases. For Cs the yellow band occurs on the longwavelength side of the forbidden transition $7S-6S$. Happer et al. [75a, d] have suggested that this band arises due to the transitions between a bound $7s\sigma$ Cs-noble-gas excited molecular state and a dissociative $6s\sigma$ ground state. The potential curves for these states calculated by Pascale and Vandeplanque [24] are shown in Fig. 7.

The origin of the emission bands under consideration may be explained if one assumes that the transition moment for $7s\sigma - 6s\sigma$ varies with the interatomic separation r and for small r it is large. Let us note that the repulsive character of potential curve for the $7s\sigma$ state of Cs-He (see Fig. 7) is consistent with the experimental fact that no yellow emission band occurs for helium.

In a further work Happer et al. [75b] have observed the same Cs yellow band in absorption. A comparison of their absorption and emission profiles for the $7s\sigma - 6s\sigma$ transition in Cs-Xe is shown in Fig. 8. Various aspects of these bands have just been

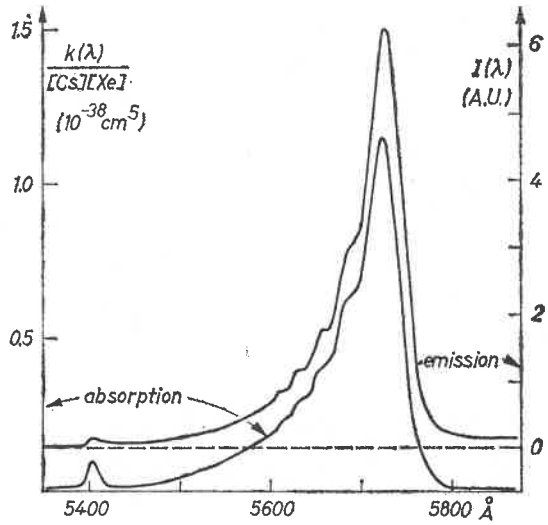

Fig. 8. Absorption and emission profiles for the $6S - 7S$ transition in Cs perturbed by Xe at the xenon pressure 2.4 atm and the cell temperature 370°C (from Ref. [75b])

discussed by Moe, Tam and Happer [75d] on the basis of the Pascale and Vandeplanque potentials. No quantitative explanation of the observed profiles of yellow bands has been, so far, reported. The UFC theory cannot be directly applicable to the $7S - 6S$ transition in Cs because the dipole moment $\mu_{if}^{(0)}$ in Eq. (2) is assumed to be independent of the interatomic separation r. It seems, however, that this restriction can be removed by including the dependence of $\mu_{if}^{(0)}$ on Condon points: $\mu_{if}^{(0)} = \mu_{if}^{(0)}(r)$. The form of this dependence is, in general case, not known. Some attempts of determining such a dependence have recently been done by Granier, Granier and Schuller [76], who performed calculations of the transition probability as a function of r for the resonance transitions $5P - 5S$ and forbidden transition $4D - 5S$ in Rb perturbed by Xe. They have found that the transition probability for $4D - 5S$, which is zero for $r \to \infty$, increases rapidly at small r.

The absorption bands corresponding to the $5S - 4D$ transitions in Rb-noble-gas mixtures have been observed by Moe et al. [75a]. To my knowledge no quantitative comparison with the calculations of Granier et al. [76] has been done as yet.

F. Wings of Stark broadened hydrogen lines

Now let me tell you briefly about some new results connected with the application of the UFC treatment to calculations of profiles in the wings of hydrogen lines broadened due to Stark effect in plasmas. It is well known that non-adiabatic effects caused by collisions of radiating atom with electrons are very important for the core of hydrogen lines and can be precisely taken into account using the generalized impact theory of Baranger [12, 28] and Kolb and Griem [29, 30]. On the other hand, experiments of Boldt and Cooper [31], Elton and Griem [32] and Schlüter and Avila [33] showed that in the

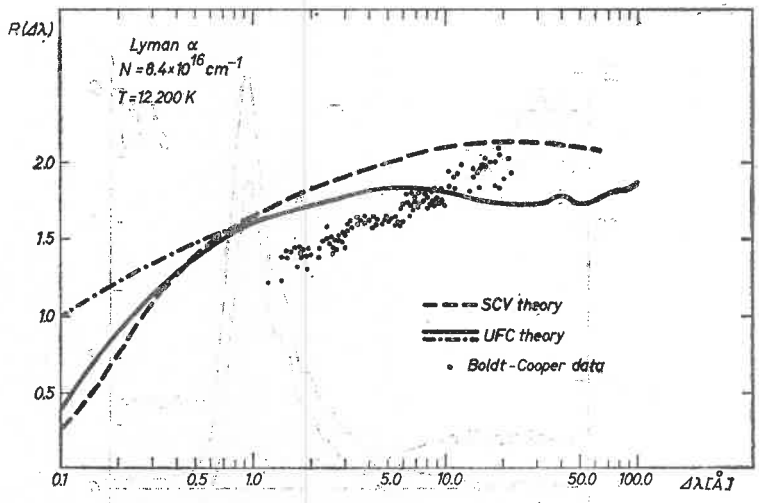

Fig. 9. Ratio $R(\Delta\lambda) = I(\Delta\lambda)/(\Delta\lambda)$ (of the total intensity distribution $I(\Delta\lambda)$ to the Holtsmark distribution $I_H(\Delta\lambda)$) as a function of $\Delta\lambda \equiv \lambda - \lambda_0$ for the Stark broadened Lyman-α line (λ_0 = 1215 Å) for the density of electrons $N_e = 8.4 \times 10^{16}$ cm^{-3} and $T = 12200$ K. Dashed curve — results of the non-adiabatic theory of Smith, Cooper and Vidal [36]. Full line — purely adiabatic UFC calculations with γ in Eq. (4) computed from the adiabatic impact theory for linear Stark broadening. Curve —·— corresponds to UFC calculations with γ computed from the approximation of H. R. Griem, *Astrophys. J.* **132**, 883 (1960). Experimental points are from Ref. [31]

intermediate frequency range the experimental profiles of Stark-broadened H lines did not agree with those obtained from the generalized impact theory. In 1968 Schlüter [34] performed the analysis of an extensive experimental material collected by him and by the authors of papers [31–32] and showed that:

1. In far wings both the ions and electrons give rise to a quasistatic Holtsmark profile $I_H(x) = C_2|x|^{-5/2}$, which is typically adiabatic in nature (C_2 is the linear Stark broadening constant);

2. The transition from the impact to quasistatic broadening by electrons can be understood basically as a transition from motional and non-adiabatic to quasistatic and adiabatic broadening.

Similar conclusion was drawn by Kogan and Lisitsa [35]. Therefore, it seemed justified to apply the UFC profile in Eq. (4) even for the case of Stark broadened H lines everywhere except in the core, where the generalized impact theory should be used.

For the linear Stark broadening the adiabatic potential difference in Eq. (10) is of the form $\Delta V(r) = \hbar C_2 r^{-2}$. Applying this $\Delta V(r)$ to the UFC formula in Eq. (11) the present author has recently completed calculations of the shape of Stark broadened wings of the Lyman-α line of hydrogen for conditions corresponding to the experiments of Boldt and Cooper [31] and Elton and Griem [32]. Results of these calculations are shown in Figs 9 and 10, where the computed UFC values of the ratio $R(x) = I(x)/I_H(x)$ (of the total intensity distribution $I(x)$ to the Holtsmark distribution $I_H(x)$) are compared with those

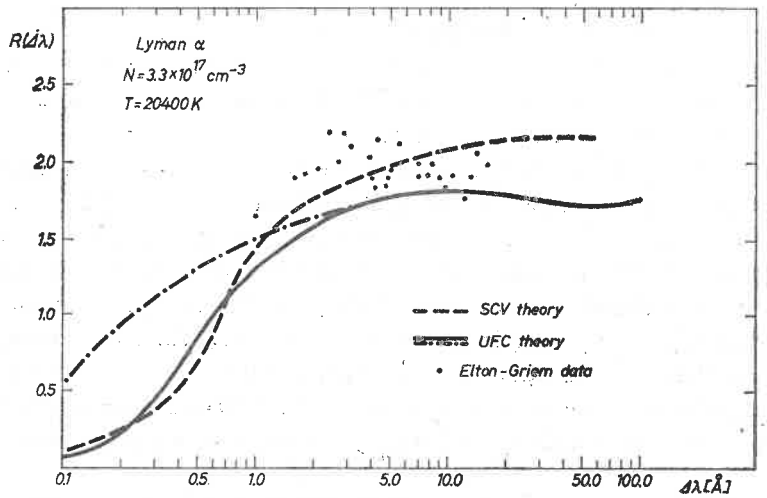

Fig. 10. Ratio $R(\Delta\lambda)$ for the Lyman-α line of H for $N_e = 3.3 \times 10^{17}$ cm^{-3} and $T = 20400$ K. Dashed curve — nonadiabatic theory of Smith, Cooper and Vidal [36]. Full line — pure adiabatic UFC calculations, with γ computed from the adiabatic impact theory for linear Stark broadening. Curve —·— corresponds to UFC calculations with γ computed from the Griem approximation (*Astrophys. J.* **132**, 883 (1960))

obtained from the non-adiabatic unified classical-path theory of Smith, Cooper and Vidal (SCV) [36] and with experiment. As it is seen the UFC results differ from those of SCV, though the discrepancy is of a reasonable size. We can also see that the UFC as well as SCV values of $R(x)$ are in a reasonable agreement with experiment.

Let us mention that the full quantum one-perturber treatment of the Stark broadening of hydrogen lines has recently been studied in a series of papers by Van Regemorter and his coworkers at Meudon [37]. The connections between the full quantum and classical path treatments of Stark broadening of H lines have just been investigated by Baryshnikov and Lisitsa [78].

4. Line core

A. Lorentzian broadening

A great number of papers dealt with the analysis of the central part of the line, i.e. for $x \approx 0$, where the impact approximation is valid. As was shown in Ref. [7] for $x \to 0$ Eq. (6) yields $F(x) \to \frac{1}{2}\gamma$ so that the UFC profile in Eq. (4) becomes there identical with the Lorentzian distribution of the adiabatic impact theory.

I wish to emphasize, however, that in contradiction to the wings in the centre of the line non-adiabatic effects may be very important. In general case the interaction between atoms is essentially anisotropic so that the different potential curves corresponding to various orientations of the angular momenta of the colliding atoms with respect to the internuclear axis have to be taken into account. The collision induced transitions between potential curves corresponding to different values of the quantum number m_J may play sometimes a very essential role, in particular those caused by the rotation of the interatomic axis during the collision. The orientation effects can be included using the scattering S-matrix formalism with the classical path approximation as described by Tsao and Curnutte [39] on the basis of Anderson's theory [38]. This formalism yields the Lorentzian shape of the line with halfwidth γ and shift Δ expressed by elements of the S-matrix suitably averaged over all allowed combinations of the m_J-states.

In recent years several calculations based on the S-matrix formalism and the classical path approximation have appeared. Lewis et al. [40] and Roueff [41] have calculated γ and Δ for the Na D lines broadened by atomic hydrogen using the potentials given by the valence configuration interaction model. The width and shift of the Na D doublet broadened by He have been calculated by Lewis and McNamara [42] using the Na-He potentials calculated by Baylis [23]. In the paper by Roueff [43] the broadening of the same lines by He has been calculated on the basis of an exchange potential model given by Nikitin [44]. Recent experiment of Deleage et al. [45a] for Na D lines broadened by He at low pressures has shown an excellent agreement between the calculated and measured results.

Using the Hund molecular coupling scheme Kunth et al. [52] have shown that the inclusion of the rotational coupling of levels during the collision allows a correct description of the behaviour of different lines in a multiplet. In particular, they were able to explain quantitatively the experimental result that although the fine structure splittings of the potassium $5^2P_{3/2,\,1/2}$ and sodium $3^2P_{3/2,\,1/2}$ levels are almost equal, the lines of the doublets emitted from these two levels of sodium ($3P-3S$) are practically equally broadened by helium at temperature 450°K (1.52 and 1.62×10^{-9} rad s^{-1} cm^3 for D_1 and D_2 line, respectively), while the broadening of potassium lines ($5P-4S$) is different (4.65 and 6.65×10^{-9} rad s^{-1} cm^3 for D_1 and D_2).

Quite recently Wilson and Shimoni [46] reported results of their calculations of the width and shift of Na D lines broadened by He based on the full quantum-mechanical impact theory of Baranger [12]. They used the Baylis potential [23] and the combined potential of Baylis and Krauss et al. [47] and found that the full quantum-mechanical results are in good agreement with the classical path calculations.

The treatment of Lewis and McNamara [42] has just been extended in Newcastle by Lwin, McCartan and Lewis [51, 55] to include the broadening and shift of the Na D lines by Ne, Ar and Xe. These calculations showed very good agreement with the experimental results of McCartan and Farr [56]. Another interesting results of these calculations [55] is that the temperature dependence for the broadening by small perturbers (H, Ne, He) is $\gamma \sim T^{0.4}$. (If the interactions were purely van der Waals, then $\gamma \sim T^{0.3}$.)

The influence of orientation effects on the pressure broadening of alkali doublets has

also been studied within the framework of the classical path approximation by Schuller et al. [48–50]. Using the Schuller treatment [48] Granier et al. [50] have found a good agreement of experimental values of γ and Δ of Rb and Cs resonance lines perturbed by noble gases with those calculated on the basis of the Baylis [23] and Pascale and Vandeplanque [24] potentials.

The first calculation of the broadening and shift of the resonance line of Li perturbed by He was carried out by Bottcher et al. [53] on the basis of Baranger's impact theory. Recent experiment performed by Smith and Collins [54] in Oxford gave results which were

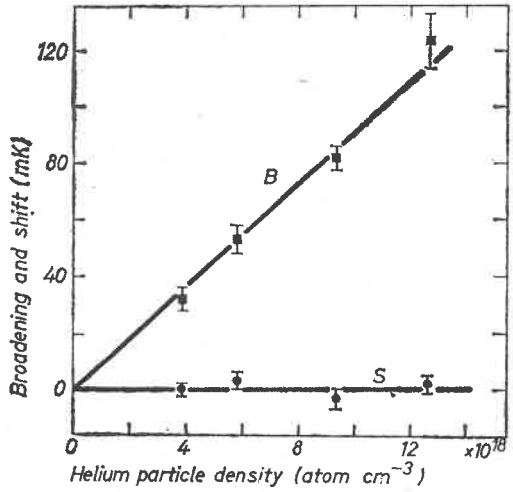

Fig. 11. Collision broadening (line B) and shift (line S) as a function of perturbers density for the resonance line of Li broadened by He (from Ref. [54])

in reasonable agreement with these calculations. An interesting result of this experiment is the lack of the shift, which may be regarded as an evidence of the strong influence of the repulsive part of the Li-He interatomic potential on the Li resonance line. Experimental results of Smith and Collins for the width and shift as a function of helium density are plotted in Fig. 11.

The calculations of Bottcher et al. [53] yielded for the shift of the Li resonance line due to the pressure of helium the value $\Delta/N = 0.05 \times 10^{-9}$ rad s^{-1} cm^3 (red shift), while the experimental result [54] is $\Delta/N = (0.00 \pm 0.05) \times 10^{-9}$ rad s^{-1} cm^3.

The purely adiabatic calculations based on the Linsholm-Foley impact theory have recently been completed at Louisville, Kentucky by Kielkopf [57], who tabulated the width and shift for the first three principal series lines of each alkali atom perturbed by noble gases. He has used semiempirical potentials and shown that the results obtained from the adiabatic impact theory should be most reliable for the case of broadening by higher noble gases, such as Kr and Xe, since for these gases the attractive interactions dominate the uncertain repulsive interaction.

B. Asymmetry in the line core

Recent advances in the experimental technique of determining the line shape [58, 59] have permitted measurements which reveal that deviations from the Lorentzian distribution may occur sometimes even in the strictly impact region, i. e. in the line centre. Such asymmetrical broadening has been observed in absorption first by Smith [60] in Oxford for the resonance line 4227 Å of calcium perturbed by Ar, Kr and Xe under pressures up to one atmosphere and was attributed by him to breakdown of the impact approximation. McCartan [61] in Newcastle has found deviations from the Lorentzian shape on the red side of the potassium lines 4044 and 4047 Å perturbed by Ar and Kr. Both Smith and McCartan have noted, however, that when perturbing gas is helium the lines are quite symmetric in the impact region.

Smith [62] has recently found asymmetrical distribution in the central parts of the 4555 and 4593 Å lines of Cs perturbed by Ar and Xe. A detailed analysis performed by him has shown that both for calcium and caesium lines [60, 62] the observed asymmetries can be satisfactorily described by the asymmetrical profile derived by Anderson and Talman [63] under assumption of the van der Waals potential.

On the other hand Baylis and the present author [64] have just shown that the non-Lorentzian behaviour in the core of the line can be obtained from the UFC profile in Eq. (4) if $H_l(x)$ in Eq. (7) is expanded in powers of x. In the first approximation the function $F(x)$ in Eq. (4) may be then written as

$$F(x) = \frac{\gamma}{2} + \alpha x, \tag{15}$$

where the asymmetry factor α for the van der Waals interaction $\Delta V(r) = \hbar C_6 r^{-6}$ is given by

$$\alpha = 0.1183 \left(\frac{\gamma^3}{N v^3}\right)^{1/2}, \tag{16}$$

which agrees well with the Anderson-Talman result

$$\alpha = 2.63 N \left(\frac{C_6}{v}\right)^{3/5} \tag{17}$$

and with Smith's experimental data (v — the mean relative velocity of colliding atoms).

It should be noted that an asymmetry similar to that discussed above was found by Kielkopf [18b] and by Royer and Allard [69] in their classical phase-shift calculations of total line profiles.

A number of theoretical papers have recently drawn attention to a further possible cause of the asymmetry of spectral lines [65–68]. In the experimental analysis of line shapes in the low pressure region one assumes that the resultant line shape is described by the well known Voigt profile, i. e. the convolution of the Doppler and Lorentzian profiles, which are treated as statistically independent. If the correlation between Doppler and pressure broadening is taken into account then as was shown [65–68] deviations from the Voigt function giving rise to line asymmetry may occur. The magnitude of this asym-

metry depends on the ratio of the mass of the perturber to that of the radiator (κ). Ward, Cooper and Smith [68] have pointed out that the correlation effects are not expected to be noticeable if κ is less than 5. For most of the published line broadening experiments $\kappa < 5$ and this justifies the use of the Voigt profile in their analysis. It is also clear that the asymmetry observed by Smith [60, 62] in his experiments on Ca and Cs lines cannot be caused by the correlation effects ($\kappa = 0.3$ for Cs+Ar and $\kappa = 1$ for Cs+Xe).

The first experimental evidence of correlation effects has just been found by McCartan and Lwin [70] for the resonance line 6707 Å of lithium perturbed by Xe ($\kappa = 19$). They have shown that the blue side of this line may be fit to a Voigt profile but the derived width parameters are not satisfactory, as can be seen in Fig. 12. The Gaussian widths

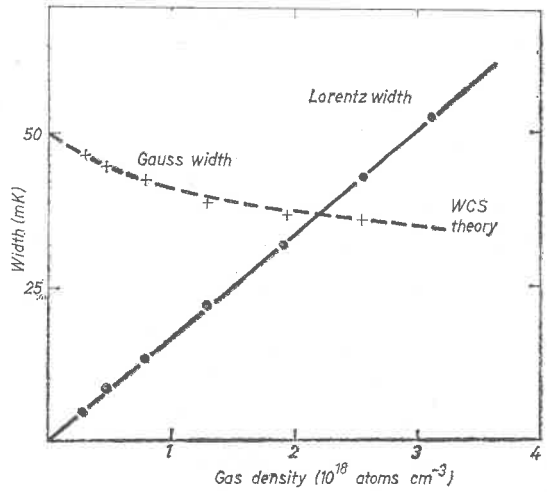

Fig. 12. The Voigt analysis of the lithium resonance lines broadened by various pressures of xenon. The Gaussian widths (+++) as determined from the 5% height of the profile are in excellent agreement with the predictions of Ward, Cooper and Smith (— — —) (from Ref. [70])

depend on xenon pressure and differ from the value expected from the measurements of the temperature of the absorption cell filled with xenon. Fig. 12 shows that the values of the Gaussian widths determined from the 5% height of the line profile are in excellent agreement with those computed by Ward, Cooper and Smith [68]. It should also be emphasized that experiments of McCartan and Lwin have shown that when the 6707 Å line of Li is perturbed by helium ($\kappa = 0.6$) the complete profile fits a Voigt shape exactly with the Gaussian width independent of pressure. An analysis of line shape for other noble gases: neon ($\kappa = 2.9$), argon ($\kappa = 5.9$) and krypton ($\kappa = 12$) revealed that the deviation from the Voigt profile becomes more noticeable as the perturber mass is increased. The main conclusion of McCartan and Lwin's work is that the high resolution investigation of line shape when κ is greater than about 5 can give direct evidence of correlation effects which are in excellent agreement with the theory of Ward, Cooper and Smith. The influence of correlation effects on atomic line shapes may not have been observed in previous experiments because of lack of resolution and a restriction to small values of κ.

Let us mention in the end that correlation between Doppler and pressure broadening are of great importance in laser spectroscopy as shown in papers of Berman and Lamb [67, 71], Cooper, Smith et al. [68, 72] and Fiutak et al. [66]. These papers have taken into account both the "energy-level perturbation" and "velocity-changing" aspects of atomic collisions. Both these aspects appear to be very essential also in studies of the influence of collisions on the line shapes associated with Doppler-free two-photon spectroscopy. A theory of collision broadening in the two-photon spectroscopy has just been developed by Berman [73] and by Ben-Reuven et al. [74]. They have demonstrated that systematic two-photon line shape investigations can provide a new and important probe of pressure effects in atomic and molecular systems.

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