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High density self-broadening of the first xenon and krypton resonance line (*)

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Abstract. — Self-broadening of the 146.96 nm xenon line and 123.58 nm krypton line is studied in the density range 1-100 amagat (2.7 × 10^{19} – 2.7 × 10^{21} at.cm^{-3}). The absorption profile is deduced from reflection experiments by a modified Kramers-Kröng analysis. A detailed discussion of the criteria for validity of available theories is given, allowing the determination of the extent to which the cases studied are related to many-body interactions and/or pure resonance forces. The quasistatic theory, in the nearest neighbour approximation, is shown to be valid for interpreting the far wings. Thus it is possible at increasing density, to underline the specific effect of the various kinds of forces: resonance, Van der Waals and repulsive, and to specify the 1_u excited state potential which is found weakly attractive for Xe_2 and Kr_2.

1. Introduction. — While many studies have been devoted to atomic line broadening by collisions with foreign gas, in either the low density or the high density range, few experiments are reported in the field of self-broadening [1] most of them in the low density range.

Such a situation may be explained by both theoretical and experimental difficulties.

From the theoretical point of view, when one tries to interpret the whole profile at high density, the main problem arises from the well-known non-additive character of the resonant interaction [2].

Experimental studies of atomic line broadening are restricted, for several reasons, to metallic vapours or rare gases. Pure metallic vapours require high temperatures and high pressures and only mercury has been studied at densities beyond 1 amagat [3-6] (1). On the other hand, rare gases have their resonance lines in the vacuum ultraviolet and the lack of transparent materials prevents quantitative work on line profiles below 105 nm; thus, high density investigations are now restricted to the first resonance lines of krypton and xenon and, although the experimental conditions remain difficult, recent instrumental improvements allow fairly accurate measurements.

Another more fundamental difficulty lies in the very strong absorption at the line centre of a pure high density gas (§ 5). Accordingly, transmission measurements cannot yield the whole profile, although the shift may be attained by unusual transmission techniques [10, 11]. Actually, such a strong absorp-


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(1) In the case of xenon, 1 amagat ≡ 2.706 \times 10^{19} \text{ at.cm}^{-3} (Ref. [7]), and in the case of krypton, 1 amagat ≡ 2.695 \times 10^{19} \text{ at.cm}^{-3} (Ref. [8]).

For a general definition of the amagat unit, see, for instance Jer-rard et al. [9].
tion is associated with the so-called selective — or specular — reflection, a phenomenon first observed by Wood [12], which consists of a coherent diffusion of the incident light at sufficient density of the absorbing medium. The properties of the selective reflection are well-known [13-15], in particular, the reflectance of the medium may be expressed as a function of its complex refractive index by Fresnel's formula which, at normal incidence, yields

\[ R = \frac{(n' - n)^2 + k^2}{(n' + n)^2 + k^2} \]  

\( n - ik \) being the complex refractive index of the absorbing medium and \( n' \) the real refractive index of the transparent window of the cell. The index of absorption \( k \) is related to the absorption coefficient \( \alpha \) by the relation \( k = \alpha x/4 \pi \). But any interpretation of the data requires the knowledge of \( n \) and \( k \) which have to be deduced from \( R \)-data by a mathematical analysis. This is the main difference as compared with direct transmittance measurements.

At normal incidence the method based on Kramers-Krönig integrals, suitably modified, appears as the only type of mathematical treatment which does not rest on an a priori chosen model. As far as we know, this procedure has never been applied to line broadening studies and \( R \)-data have been treated [3, 4, 14] in term of the semi-classical dispersion formulae, based on the harmonic oscillator model (Lorentzian shape for \( nk \)).

The present paper reports normal incidence reflectance measurements performed on xenon and krypton at high densities, in the vicinity of their first resonance lines. It has been possible to study experimentally the xenon 'line continuously from the gas phase up to the liquid phase \((T_c = 16.60^\circ C, P_c = 58.40 \text{ bar}) [17]\) and to observe the onset of excitonic phenomena in the dense fluid (appearance density \( \sim 180 \text{ amagat} \)). We will restrict ourselves here to densities below 100 amagat where interpretation in terms of interatomic potentials is possible.

At each density, the whole profile is obtained from \( R \)-data by the above mentioned Kramers-Krönig analysis.

Having briefly recalled the main theoretical developments, we discuss their applicability according to the type of force considered, the frequency range and the density range. This allows us to define the extent to which many-body interactions have to be taken into account. Finally, we show that a large part of the profile may be interpreted in the frame of the quasistatic theory (QST) in the nearest neighbour approximation (NNA). Thus valuable information about excited interatomic potentials can be obtained from wing data.

2. Theory. — In this section, we recall briefly the main theoretical results to be used for the interpretation of the present experimental data. Note that in the density range implied, Doppler width may be neglected compared with the broadening effects of atomic interactions.

Theories have developed mainly along two lines, namely impact [20] and quasistatic theories [21, 22], corresponding to complementary frequency ranges (see below § 3.2). Accordingly, we are led to distinguish between the line centre and the wings.

2.1 Line Centre. — 2.1.1 Low density case. — Impact theories, valid at low density and in the vicinity of the line centre, predict a Lorentzian shape whatever the potential considered [23], so that measurements in the line centre provide a test of a kind of potential curves rather than an actual determination of these curves [24-27].

In the case of a transition with a high oscillator strength \( f \), the effect of forces other than resonance is negligible and the broadening law is given by (2)

\[ \Delta \nu_{1/2} = \frac{K \alpha^2 fN}{8 \pi^2 \sqrt{3 \epsilon_0 m v_0}} \] (MKSA units)

where \( N \) is the density, \( m \) and \( q_e \) the electronic mass and charge respectively ; \( K \) is a constant whose value is somewhat dependent upon the various theoretical approaches (Table 1).

| Table 1. — Theoretical values for \( K \). |
|-----------------|-----------------|-----------------|
| Weisskopf       | (1933) [20]     | 1.73            |
| Margenau and Watson | (1936) [2]     | 1.81            |
| Fursov and Vlasov | (1936) [28]    | 2.31            |
| Lindholm        | (1945) [23]     | 2.72            |
| Foley           | (1946) [29]     | 1.81            |
| Byron and Foley | (1964) [30]     | 1.93            |
| Ali and Griem   | (1965) [31]     | 2.07            |
| Omont           | (1966-68) [32]  | 2.08            |
| Kazantzev       | (1967) [33]     | 2.08            |
| Vdovin and Galitskii | (1967) [34]  | 2.01            |
| Mead            | (1968) [36]     | 2.43            |
| Berman and Lamb | (1969) [35]     | 2.07            |
| Nowotny         | (1971) [38]     | 1.81            |
| Carrington et al. | (1973) [37]   | 2.08            |
| Zaidi (*)       | (1975) [39]     | 1.81 < K < 2.72 |

(*) \( K \) function of \( Nf \) (from the impact limit to the quasistatic limit).

Low density line centre measurements show a fair agreement with the more recent impact values of \( K \) [40]; the large discrepancies appearing in some cases have been critically reviewed by Exton [41].
The situation where resonance forces prevail is a specific one since a Lorentzian shape is predicted in the impact as well as in the quasistatic limit (in the nearest neighbour approximation).

2.1.2 High density case. — In the density range \( \rho \gtrsim 1 \) amagat, the impact approximation fails (§ 3) and the line centre must be described by taking into account many-body effects. Non-additivity of resonance forces is a major difficulty and the problem has to be tackled in a very general way. Apart from the early work of Holtsmark [42] based on too crude an approximation [43], various approaches have been tried using either the resolvent method [44] or many-body techniques [34, 39, 45-48]. However, most of them remain formal or find, as a limit, the impact theory result. The recent work of Zaidi [49], founded on the concept of shielded interactions and the use of propagator techniques, represents the first attempt to solve the high density resonant case. It leads to a generalized Lorentzian expression for the susceptibility of the absorbing medium

\[
\chi(\omega) = \frac{-2\pi NC_3}{\Delta\omega - \Delta_L - \Sigma(\Delta\omega)}
\]

(3)

where \( \Delta_L \) is the Lorentz shift (see § 5.2.3); \( C_3 \) corresponds to the resonant \( C_3 \) \( r^{-3} \) term of the interatomic potential and is related to the oscillator strength by the following formula (2):

\[
C_3 = \frac{q_e^2 f}{32\pi^3 \varepsilon_0 m v_0} \quad (\text{MKSA})
\]

(4)

\( \Sigma(\Delta\omega) \) is a complex term, referred to as self-energy, whose imaginary part is the principal cause of the departure of \( \text{Im}(\chi) \) from a Lorentzian shape.

Two main features are predicted in this work:

(i) A rate of broadening versus density, smaller than the linear law in the range where the binary collision approximation is no longer valid.

(ii) A correlative asymmetrical development of the line shape.

Unfortunately, only resonance forces, i.e. long distance forces, are taken into account, and since Van der Waals forces are known to play a major part in short distance interactions, this appears as a severe limitation to the applicability to real situations. Thus only strong transitions can be dealt with since, otherwise, simultaneous interactions will set up at densities where the influence of Van der Waals forces extends up to the line centre (see § 3.4).

2.2 Line wings. — In the wings of the line, impact theories fail but they are relayed by quasistatic ones (QST) which disregard the trajectory and collision concepts (see below § 3). Then, the atoms being considered at rest, the line shape is determined by the statistical distribution of the distances of atoms surrounding the excited one.

The treatment is much simplified if it is further assumed that the perturbation is dictated by the nearest neighbour [21] (nearest neighbour approximation referred to as NNA). Then the intensity distribution is proportional to

\[
P(v) = \frac{4\pi N}{3} \sum a_i \left| \frac{dr_i^3}{dv} \right|
\]

(5)

\( r_i \) are distances where the difference potential

\[
\Delta V_i(r) = V_i(r) - V_i(r)
\]

is equal to \( hv \) \(^{(3)}\) and \( a_i \) are the respective probabilities of the implied excited states.

Then the index of absorption is directly related to \( P(v) \) by

\[
k(v) = \frac{\lambda z(v)}{4\pi} = \frac{q_e^2 f N}{16\pi\varepsilon_0 m v} P(v)
\]

(6)

Eq. (6) may be written, using eq. (5)

\[
k(v) = \frac{h B q_e^2 N^2 f}{12 m v_0} \sum a_i A(r_i) \left| \frac{3 r^2}{d(\Delta V)/dr} \right|
\]

(7)

where are introduced, for the sake of generality, the Boltzmann factor \( B \) (§ 3.3) and the term \( A(r_i)/A(\infty) \) which represents the relative variation of the transition dipole moment with internuclear distance.

Eq. (5) predicts an infinite intensity at \( r \) values where \( d(\Delta V)/dr \) vanishes (satellite bands), a physically meaningless result which can be corrected either by taking into account the collision time [50-52] or by a Franck-Condon approach [53, 54]. This procedure leads to a realistic satellite shape without affecting its position noticeably. Another feature of satellite bands is a sharp decrease of intensity beyond the maximum so that, in practice, it is often possible to separate the contribution of the various molecular states involved (see § 5).

When the difference potential \( \Delta V(r) \) is a single-valued function of \( r \), NNA yields a one-to-one correspondence \( I(v) \leftrightarrow \Delta V(r) \) from which follows a simple and direct method of determination of the difference potential, upon which many recent works are based [55-61]. The method can be applied to self-broadening studies since, as shown below, NNA remains valid in selected spectral ranges. For this purpose it is convenient to adopt the following expression of the difference potential:

\[
\Delta V_M(r) = h \gamma_M |C_3|^2 r^3 - C_6 |M|^4 r^6 + C_12 |M|^6 r^{12}
\]

(8)

with \( \gamma_M = -2 \) if \( M = 0 \) and \( \gamma_M = 1 \) if \( M = \pm 1 \) (\( M \) being the magnetic quantum number); the resonant term \( \gamma_M |C_3|^2 r^3 \) has been added to the well-known Lennard-Jones potential. This allows simple calculations and also takes into account, in a realistic

\(^{(3)}\) In the following the origin of frequency will be taken at \( \nu_o \).
way, the triple effect of resonance, Van der Waals and higher order overlap forces in the interatomic distance range involved in our experiments.

3. Validity criteria. — In paragraph 2, we recalled some theoretical aspects and evoked the validity of various approximations in terms of frequency and density. The purpose of the present section is to discuss more quantitatively the ranges of validity of these approximations.

3.1 Binary Collision (Density Range). — Binary collision approximations can be retained at densities where one atom at most lies in the Weisskoff sphere surrounding the active atom. In the case of strong transitions (large values of $C_3$) this sphere is unambiguously defined by its radius $V$ where $V$ is the mean velocity of the atoms. As verified a posteriori in our cases, Van der Waals forces can be disregarded in the definition of $\rho_w$.

From $f$-values given in paragraph 5.1 and from eq. (4), we find,

$\rho_w$(Xe 147.0) = 45 Å

$\rho_w$(Kr 123.6) = 33 Å

Such values correspond to the average interatomic distance in a gas at a density $N_L \sim \rho_w^{-3} \leq 1$ amagat. Thus, we may conclude that the condition for binary collision approximation is never fulfilled in the density range of our measurements.

3.2 Frequency Range. — According to Holstein's[62] and Sobel'man's[63] works, impact theories apply in the line centre, whereas quasistatic theories apply in the wings (see also Gallagher[57]). Then a frequency limit $\nu_L$ is introduced, making the separation between the two descriptions. Such a result comes out directly from the discussion of the behaviour of the intensity, given by the square Fourier amplitude of the time varying oscillator, in the two opposite cases $\nu \gg 1/\tau_c$ and $\nu \ll 1/\tau_c$, where $\tau_c$ is the typical duration of a collision. $\nu_L$, in the cases of interest to us, is well defined by taking into account resonance forces alone

$$|\nu_L| = |2 \nu_c| = \frac{C_3^{3/2}}{\rho_w^{1/2}}.$$ (10)

It is found that $|\Delta \nu_L| \sim 4 \times 10^{-3}$ nm for both Xe 147 nm and Kr 123.6 nm lines (*). As will be shown later on, in the density range of the reported experiments, the broadening is such that the major part of the profile is in the validity range of the quasistatic assumption.

3.3 Nearest Neighbour Approximation. — In the literature, NNA is most often restricted to low enough densities. In fact, Kuhn gave the first quantitative discussion of the question and showed that, in the frame of QST, the larger the frequency shift, the higher the probability that the perturbation be induced by one instead of several perturbers [21]. Relying on that result, we propose the following simple validity criterion for the frequency range of NNA:

$$|\nu_{\text{NNA}}| \gg \frac{\Delta V(\bar{r})}{\hbar}$$ (11)

where $\Delta V(\bar{r})$ is the value of the difference potential at the mean interatomic distance. Inequality (11) simply means that one need consider a frequency range corresponding to a large departure from a fixed regular distribution, a situation where Kuhn's result is applicable.

In fact, the preceding criterion does not cover all possible situations and must be amended by the following considerations:

(i) The Boltzmann factor

$$B = \exp(-V_g/kT)$$ (12)

introduces a cut off in the approach distance between atoms in their ground state. Let $\sigma$ be the distance of the turning point and $\nu_g$ the corresponding frequency. For frequencies $\nu$ such that $|\nu| > |\nu_g|$, the Boltzmann factor strongly decreases the probability that the perturbation be induced by a simple perturber at short distance so that Kuhn's reasoning may progressively fail at increasing $|\nu| (>|\nu_g|)$.

(ii) Another case may occur, illustrated in figure 1. For a point such as M, the frequency $\nu$ is positive (blue side) and does not fulfill the condition (11); nevertheless, NNA is valid because the whole blue side corresponds to only close approach distance and $B$ plays no restrictive part.

Thus we see that, when QST + NNA (thereafter referred to as NNQST) is used, an a posteriori control of the range of interatomic distance corresponding to the interpreted wing data has to be done.

Let us now illustrate the above condition in two particular cases of monotonic potential curves:

a) Resonant interactions. — The $C_3 r^{-3}$ potential law yields from eq. (11)

$$|\nu_{\text{NNA}}| \gg C_3 \bar{r}^{-3} \sim C_3 N.$$ (13)

As, in this case, the HWHM is typically from eq. (2) and (4) and table I

$$\delta \nu_{1/2}(R, B) \sim 2 \pi NC_3$$ (14)

(R = red, B = blue).

(*) Actually, because of the factor $\gamma$ in the term arising from resonance forces (eq. (8)), different limit frequencies could be introduced for the red and blue sides, but in a discussion of validity criteria, this distinction may be forgotten.
We may write

\[ |v_{\text{NNA}}| \geq \frac{\delta v_{1/2}(R, B)}{2 \pi}. \]  

(15)

b) Van der Waals interactions. Then we have

\[ |v_{\text{NNA}}| \geq C_6 \bar{r}^{-6} \sim C_6 N^2. \]  

(16)

The true profile is approximated by the quasistatic profile given by Margenau [22]. Disregarding the physically meaningless blue wing of this profile (no intensity at \( v > v_0 \)), we then write for the red wing

\[ \delta v_{1/2}(R) \sim 20 C_6 N^2 \]  

(17)

from which we get

\[ |v_{\text{NNA}}| \geq \frac{\delta v_{1/2}(R)}{20}. \]  

(18)

For both particular cases, NNA is expected to be valid up to nearly the half-maximum of the line. Consequently, from the very simple theoretical background of NNQSST it is possible to account for the properties of a high density gas in a large spectral range, whatever kind of force is acting — resonance, Van der Waals or other.

3.4 HIGH DENSITY RESONANT CASE (\( N > N_l \)). As previously said (§ 3.1) the binary collision approximation fails in the line core if \( N > N_l \). For \( N = N_l \) the HWHM is typically

\[ \delta v_{1/2}(R, B)_L = 2 \pi N_l C_3. \]  

(14bis)

Since \( N_l = \rho_w^{-3} = (\pi/4 \pi C_3)^{3/2} \), eq. (10) yields

\[ \frac{v_L}{\delta v_{1/2}(R, B)_L} = \frac{2}{\pi^{1/2}} \approx 1. \]  

(19)

At \( N > N_l \) we get

\[ \delta v_{1/2}(R, B) > v_L \]  

(20)

and most of the profile will be relevant to the quasistatic assumption with many-body effects typically in the line centre, above the half-maximum, as illustrated in figure 2. Due to the high value reached by

\[ \text{the absorption maximum (§ 5.2.2) it is worthy of note that the many-body range can only be studied by reflection. Now an additional question arises. Can we neglect Van der Waals forces in the line centre at high densities? To answer this question, let us consider for instance } N_H = 10 N_l. \text{ Then}

\[ \delta v_{1/2}(R, B)_H = 10 \delta v_{1/2}(R, B)_L = 20 \pi N_l C_3. \]  

(21)

Following NNA, the frequencies \( \pm \delta v_{1/2}(R, B)_H \) are associated with distances:

\[ r_H = \left( \frac{C_3}{\delta v_{1/2}(R, B)} \right)^{1/3} \]  

for the blue wing, and

\[ r_H = \left( \frac{2 C_3}{\delta v_{1/2}(R, B)} \right)^{1/3} \]  

for the red wing.
From eq. (9) and (21) we then obtain for $r_H$

$$r_H \sim \left(\frac{4 \pi \nu}{c}\right)^{1/2} \varepsilon_{3}^{1/2}(20 \pi)^{-1/3}.$$  \hspace{1cm} (22)

Pure high density resonant case could be studied if

$$C_3 r_H^{-3} \gg C_6 r_H^{-6}.$$  \hspace{1cm} (23)

From eqs. (22) and (23) we therefore write the condition

$$C_3 \gg (20 \pi C_6)^{2/5} (\nu/4 \pi)^{3/5}. \hspace{1cm} (24)$$

To get an order of magnitude, let us take some typical values $C_6 = 10^{-31} \text{cm}^6 \cdot \text{s}^{-1}$, $\nu = 4 \times 10^6 \text{cm} \cdot \text{s}^{-1}$; we obtain:

$$C_3 = 1.070 \times 10^{-11} \int_{\text{abs}} \gg 2.6 \times 10^{-10} \text{cm} \cdot \text{s}^{-1}$$

or

$$\int_{\text{abs}} \gg 24.$$  \hspace{1cm} (25)

Such a condition is not really fulfilled in the present study and we may conclude that a pure high density resonant case has to be studied for high $f$-values.

4. Experiment, data analysis, discussion. —

4.1 Experiment. — The experimental methods and apparatus have already been described [16]. So we mention them briefly.

Quantitative V.U.V. measurements are performed with a double beam photometer [64] suitably modified for reflectance measurements (Fig. 3). This photometer is attached to a monochromator whose resolution is of the order of 0.04 nm; the light source is a deuterium lamp emitting a pseudo-continuum.

A typical reflectance curve is presented on figure 4. Density is accurately determined, from measured pressure and temperature (\sim ambiant temperature), with the help of the known equations of state (Xe [65]; Kr [8]).

4.2 Kramers-Krönig analysis. — In order to obtain the true absorption profile, the analysis of normal incidence reflectance data has to be performed without the preliminary choice of any model. This is allowed in principle by Kramers-Krönig analysis provided the whole reflection spectrum is known. Usually only a restricted spectral range is observed so that the method is always combined with some extrapolation procedure [66, 67].

Following an idea of Bachrach and Brown [68], Ahrenkiel [69] has developed a substractive procedure well suited to the analysis of a limited spectral range since it gives a more rapid convergence of the integral in the unobserved part of the spectrum. We have adapted Ahrenkiel's method to the case where the absorption index $k$ vanishes in the far wings on both sides of the atomic line, by adopting a doubly substractive procedure [6]. Systematic tests performed on synthetic spectra, with parameters close to real ones, have demonstrated the good accuracy of the method, even when the integration is limited to ten times the half-width of the broadened line.

4.3 Discussion. — Before proceeding further, let us discuss the part played by two specific effects which may occur in high density reflectance measurements.

4.3.1 Wall effect. — First of all, one may imagine rare gas atoms getting adsorbed on the surface or even migrating into the bulk of the transparent window. Such phenomena should yield broad absorption bands rather insensitive to pressure, which is not observed.

Secondly, one may wonder whether the window has any influence from either a collisional or a static point of view, since, at the line centre, the penetration depth of light is typically \sim 15 nm (§ 5.2.2). If, at fixed temperature, collisions with the window were the main physical process, increasing the density should not basically change the process but only
increase its rate, leaving the corresponding half-width unchanged, which is not observed. On the other hand, we have in our density range

\[ n_e > n_p \]

where \( n_p = 1/4 N V \) is the number of atoms colliding with the window per second and unit area, and \( n_e \sim N^2 \tau V \) is the number of atom-atom collisions per second in a volume \( V \) of unit section and height equal to the penetration depth, which does not change significantly with density (§ 5.2.2). Thus we may conclude that, even when the penetration depth is minimum, collisions with the window contribute a negligible amount to the observed broadened line.

Let us now look at the static point of view: if the perturbation of the atoms by the window is dominating, it will be only dependent on the atom-window distances; as the depth of penetration does not change significantly with density, the line shape would depend on an unchanged distribution of perturbation with increasing density i.e. the half width would be constant, which is not observed.

4.3.2 Molecular effects. — It is well known that a weakly attractive ground state potential leads to the existence of bound pairs among the free atoms. The corresponding molecular spectra for Xe and Kr have been observed at low density [70-74] and partially analysed. The proportion of molecules can be calculated only at low density [75]. As a very crude approximation, extrapolation of such a calculation indicates that, from 1 to 100 amagat, bound pairs could represent from 1 to 50% of the whole atoms for xenon and from 0.5 to 30% for krypton (room temperature); we may also expect effects coming from molecular complexes, trimers... In fact, the experiment does not reveal any important molecular effect so that the above estimation may appear doubtful. Actually, we must bear in mind that these molecules are weakly bound — the potential well depth is 196.3 cm\(^{-1}\) for Xe and 140.3 cm\(^{-1}\) for Kr [76] — so that they are easily dissociated by thermal collisions (at room temperature, \(3/2 kT \sim 300\) cm\(^{-1}\)). Consider now the collision frequency \( f_c \) at 100 amagat for an approach distance \( d = r_e \):

\[ f_c(Xe, Kr) \sim 5 \times 10^{11} \text{ Hz} \]

Compared to the classical vibration frequency of the molecule [77-79]

\[ \omega_v(Xe) = 17.7 \text{ cm}^{-1} \left( = 5.3 \times 10^{11} \text{ Hz} \right) \]

\[ \omega_v(Kr) = 24.0 \text{ cm}^{-1} \left( = 7.2 \times 10^{11} \text{ Hz} \right) \]

\( f_c \) is of the same order of magnitude as \( \omega_v \).

This casts some doubt on the specific nature of bound pairs at high densities as compared with the free ones, since their lifetime may be much reduced by collisions. This would explain why the molecular contribution to the spectrum is much weaker than the computed one.

5. Experimental results and interpretation. — Illustrations of the absorption profiles obtained are given in figures 5 and 6 for xenon and in figure 7 for krypton. Similar features are observed for both lines:

(i) Unsymmetrical wings, even in the low density range, with a long red wing and a steep blue one.

(ii) Appearance and development of a far blue wing at intermediate densities.

![Fig. 5. — 146.96 nm xenon line absorption profile : density 20.4 amagat, temperature 20 °C.](image)

![Fig. 6. — 146.96 nm xenon line absorption profile ; density 70 amagat, temperature 20 °C.](image)

![Fig. 7. — 123.58 nm krypton line absorption profile ; density 80.2 amagat, temperature 20 °C.](image)
5.1 INTEGRATED AREA. — The first information we can get from these profiles is the integrated area, obtained almost completely since very far wings do not contribute significantly. The well-known relation between integrated area and oscillator strength is in principle based on the assumption of Lorentzian profiles. We nevertheless tabulated the f-values deduced from this relation for various densities. No systematic variation is observed with density and the averaged values of f for both lines are in fair agreement with other determinations found in the literature (Table II). Thus we are inclined to think, at least for these strongly allowed transitions and in the internuclear distance range implied by our experiments (see Tables III and IV), that no important variation of the transition moment occurs, in agreement with Mulliken’s estimation [94] in the case of xenon. We shall therefore, adopt in the following $A(r)/A(\infty)=1$ (eq. (7)).

Table II. — Oscillator strengths associated with the 146.96 nm xenon line and 123.58 nm krypton line as determined by various investigators.

<table>
<thead>
<tr>
<th></th>
<th>Xe 146.96 nm</th>
<th>Kr 123.56 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Koch</td>
<td>0.194</td>
<td>0.266</td>
</tr>
<tr>
<td>Anderson</td>
<td>0.256</td>
<td>—</td>
</tr>
<tr>
<td>Turner</td>
<td>0.166</td>
<td>—</td>
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<tr>
<td>Wilkinson</td>
<td>0.158</td>
<td>—</td>
</tr>
<tr>
<td>Chaschina et al.</td>
<td>0.28</td>
<td>—</td>
</tr>
<tr>
<td>Vaughan</td>
<td>0.204</td>
<td>—</td>
</tr>
<tr>
<td>Griffin et al.</td>
<td>0.187</td>
<td>—</td>
</tr>
<tr>
<td>Geiger</td>
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<td>—</td>
</tr>
<tr>
<td>Natali et al.</td>
<td>0.272</td>
<td>—</td>
</tr>
<tr>
<td>Wiene et al.</td>
<td>0.214</td>
<td>—</td>
</tr>
<tr>
<td>Delage et al.</td>
<td>0.170</td>
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</tr>
<tr>
<td>Present work</td>
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<td>0.21</td>
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Theoretical

<table>
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<tr>
<th></th>
<th>Xe 146.96 nm</th>
<th>Kr 123.56 nm</th>
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<tr>
<td>Dow et al.</td>
<td>0.194</td>
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<td>Gruzdev</td>
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<td>Aymar</td>
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Table III. — Numerical values of intermolecular potentials of Xe$_2$ (origin at the respective dissociation limit).

<table>
<thead>
<tr>
<th>r (Å)</th>
<th>$V(^1\Sigma^+_g)$ (cm$^{-1}$)</th>
<th>$V(^1\Sigma^+_u)$ (cm$^{-1}$)</th>
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<tbody>
<tr>
<td>3.8</td>
<td>127</td>
<td>2900</td>
</tr>
<tr>
<td>4.0</td>
<td>101.7</td>
<td>1225</td>
</tr>
<tr>
<td>4.3</td>
<td>194.5</td>
<td>230</td>
</tr>
<tr>
<td>$r_e = 4.363$</td>
<td>196.27</td>
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<tr>
<td>4.5</td>
<td>189.8</td>
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<tr>
<td>4.7</td>
<td>166.8</td>
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<td>5.4</td>
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<td>5.8</td>
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<td>6.0</td>
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<td>11</td>
<td>0.83</td>
<td>7.6</td>
</tr>
<tr>
<td>12</td>
<td>0.49</td>
<td>6.4</td>
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</table>

Table IV. — Numerical values of intermolecular potentials of Kr$_2$ (origin at the respective dissociation limit).

5.2 LINE CENTRE. — 5.2.1 Evolution of the half-width. — The evolution of the half-width versus density is given in figures 8 and 9. Note the asymmetry of the line in the whole density range, especially in the case of xenon.

Using results obtained from wing data for the excited potential curves (§ 5.3), we may relate that asymmetry to the increasing effect of Van der Waals forces which, according to QST, reduce the blue width (they are subtractive with respect to repulsive forces)
Fig. 8. — 146.96 nm xenon line half-width versus density. Circles : FWHM ; triangles : blue HWHM ; dashed curve : extrapolation of the theoretical resonance broadening for $K = 2.07$.

Fig. 9. — 123.58 nm krypton line half-width versus density. Circles : FWHM ; triangles : blue HWHM ; dashed curve : extrapolation of the theoretical resonance broadening for $K = 2.07$.

resonance forces associated with $M = \pm 1$) and increase the red (additive effect, $M = 0$).

As already pointed out, a quantitative interpretation of the broadening exceeds the present possibility of theory on account of the simultaneous presence of two kinds of forces in this many-body case.

In the case of xenon, in the density range 1-20 amagat, we note that, despite the limited resolving power, the broadening is below the extrapolated linear impact result obtained for pure resonance broadening. Such a behaviour, we believe, could be connected to the shielded interaction concept developed by Zaidi (§ 2), the effect of which is a reduced broadening.

The krypton line does not exhibit so clear an effect, what may be ascribed both to its smaller $f$-value (smaller resonant broadening) and to the lower accuracy of measurements at corresponding shorter wavelengths.

5.2.2 Evolution of the maximum $k_M$ of the index of absorption. — In order to get an idea of the evolution of $k_M$, let us first establish a general property of Lorentzian profiles for a gas of identical atoms.

The index of absorption written

$$k = \frac{N q_e^2 f y}{8 \epsilon_0 m \omega} \frac{1}{(\omega - \omega_0)^2 + (\gamma/2)^2}$$

yields a maximum

$$k_M = \frac{N q_e^2 f}{2 \epsilon_0 m \omega y}.$$

In the resonant case, eq. (2) gives

$$\gamma = 2 \pi \Delta v_{1/2} = \frac{q_e^2}{\epsilon_0} \frac{K}{\sqrt{3}} \frac{N f C}{2 \pi m v_0}.$$

Hence

$$k_M = \frac{\sqrt{3}}{K} = \text{const.}$$

From table 1, we see that, for impact broadening, the typical value $K = 2.07$ leads to

$$k_M = 0.837$$

which corresponds to a depth of penetration $l \sim \lambda/10$.

Reciprocally, the experimental determination of $k_M$ yields $K$ without the knowledge of $f$, whereas the broadening yields $K f$.

On the other hand, in the case of very weak oscillator strength, impact Van der Waals broadening dominates and from Lindholm’s broadening law

$$\Delta v_{1/2} = 2.68 C^{2/5} \frac{q_e^2 f}{21.4 \times \pi^2 \epsilon_0 m v C^{2/5} 3/5} N$$

one would obtain

$$k_M = \frac{q_e^2 f}{21.4 \times \pi^2 \epsilon_0 m v C^{2/5} 3/5}.$$

Our experiments are performed at densities where the two-body interaction assumption is no longer valid. We observe both a broadening smaller than the extrapolated two-body resonance broadening (§ 5.2.1) and a development of the far wings. Both effects balance each other to a certain extent as far as the behaviour of $k_M$ is considered. Between 1 and 20 amagat, the average values of $k_M$ obtained are 0.88 for Xe 147.0 nm and 0.8 for Kr 123.5 nm, which are not far from the aforementioned theoretical value 0.837 valid at lower densities.

Beyond 25 amagat, the decrease of $k_M$ can be qualitatively ascribed to Van der Waals forces in a QST description. A quantitative interpretation is
5.2.3 Shift. — In figures 10 and 11 are presented shift data obtained from reflectance measurements as well as from transmission studies [11]. Note that, especially for the xenon line, transmission data are affected by a residual systematic error due to the asymmetry of the line.

From a theoretical point of view, several mechanisms have to be evoked:

(i) Resonant shift.
(ii) Lorentz shift.
(iii) Van der Waals statistical shift.

The existence of a pure resonant shift has not yet been laid on a firm ground in the impact approximation, blue, null or red shifts being predicted by the various authors quoted in table I. At low density, in the impact case, a null shift is favoured by experimental data [95].

At higher densities, the well-known local field correction in the frame of the classical dispersion theory yields the following shift (Lorentz shift [96])

$$\omega_0^2 = \omega_0^2 - \frac{Nq_e^2f}{3me_0}\left(\frac{n_0^2 + 2}{3}\right)$$

(32)

where the term in parentheses takes into account the case of dense medium [97] and was not originally included. Although applied first to solids [98] the Lorentz shift has also been considered in the case of gases [99, 100]. In the approach of Zaidi, the Lorentz term appears but its influence is reduced on account of the shielding effect.

The actually observed shift is clearly smaller than the Lorentz shift at densities below 40 amagat. Furthermore, the shift exhibits a quasiquadratic dependence leading to the conclusion that the generalized Lorentz shift given by Zaidi is not the main physical process in our case.

If one now imagines, in a rather crude approximation, that the effects of resonance forces associated with the two involved molecular states (see next §), opposite in sign, cancel each other as far as the shift is concerned, the shift can be expressed as (22):

$$\Delta\nu = \left(\frac{2\pi}{3}\right)^3 \overline{C_6} N^2$$

(33)

where $\overline{C_6}$ is an average value over the two states. The corresponding fit appears in figures 10 and 11. The obtained $\overline{C_6}$ values are fairly close to the final value deduced from wing data, so that the observed shift seems effectively related to Van der Waals forces.

5.3 Line wings. — We begin with a qualitative discussion of our results with the help of available theories and known estimations of the potential curves of Xe$_2$ and Kr$_2$.

Potential curves for the first excited states of xenon and krypton have been estimated by Mulliken [94, 101] and by Barr et al. [102] respectively. Four molecular states $0_u^+, 1_u^-, 1_g^-, 0_e^-$ are correlated with the first excited state implied here, i.e. $6s(3/2)^+$ for Xe
and 5 s(3/2)\(^{\text{I}}\) for Kr. Only 0\(^{\text{u}}\) and 1\(_{\text{u}}\) states, corresponding to allowed transitions with the X \(^{1}\Sigma_{\text{g}}^{+}\) ground state, will be considered in the following. Mulliken (followed by Barr et al. for Kr) concludes that the 0\(^{\text{u}}\) state is fairly attractive with the estimated parameters

\[
r_{\text{e}} \sim 3.25 \text{ Å} \quad \varepsilon \sim 5 \text{ 600 cm}^{-1}
\]

whereas he is inclined to attribute a purely repulsive character to the 1\(_{\text{u}}\) state. On the one hand, as a consequence of the attractive 0\(^{\text{u}}\) state, a long red wing is expected from NNQST. Such a wing is indeed observed (Figs. 5-7). On the other hand, the assumption of a purely repulsive difference potential

\[
\Delta V = V_{1\text{u}} - V_{0\text{u}}
\]

— an assumption less restrictive than a purely repulsive 1\(_{\text{u}}\) state — is incompatible with our experimental results for the following reasons:

(i) The integrated area on the blue side would have to be larger than the area on the red, because of the respective weights of the two molecular states. This is not the case.

(ii) The long blue wing observed at rather high density (Figs. 6 and 7) is missing at low density where a steep blue edge is observed instead.

(iii) The quasiquadratic red shift could not be explained (§ 5.2.3).

Thus are we led, in the case of 1\(_{\text{u}}\) state, to adopt a negative \(r^{-6}\) term in the difference potential in eq. (8):

\[
\Delta V_{1\text{u}} = \hbar \left( C_{3} - \frac{C_{6}}{r^{6}} + \frac{C_{12}}{r^{12}} \right)
\]

with \(C_{3} \geq 0, C_{6} \geq 0, C_{12} > 0\).

The negative term has to be large enough both to solve the above mentioned difficulties and to lower the \(\eta\) value (Fig. 12) to an extent compatible with

\[
\eta < 30 \text{ cm}^{-1}
\]

the absence of a blue satellite. The calculation shows that this condition implies \(\varepsilon \leq 0\):

— if one assumes \(|\varepsilon| \sim 0\), the fit of the blue wing by the calculation given in the following, would lead to an \(\eta\) value large enough for the appearance of a blue satellite;

— if one assumes \(|\varepsilon| > 30 \text{ cm}^{-1}\), a red satellite would appear, which is not the case for the 147 nm xenon line, whereas preliminary results indicate such a close red satellite for the 129.5 nm xenon line [6].

Therefore, the true value of \(|\varepsilon|\) seems to be around 15 cm\(^{-1}\). Hence we may conclude that the 1\(_{\text{u}}\) state is not purely repulsive and, therefore, that the blue molecular system observed at low density very close to the atomic line [71] is correlated to the 1\(_{\text{u}}\) state. Actually, although the proximity of the atomic line has prevented complete observation and vibrational labelling of this system, the spectral range and vibrational spacings of the molecular system are quite compatible with our final potential shape.

The same discussion in the case of Kr confirms that the blue molecular system observed by Tanaka et al. [73] is also related to the 1\(_{\text{u}}\) state as suggested by the authors.

We can draw another conclusion regarding the high density profiles: apart from a narrow central region (\(|v| \sim |\varepsilon|\), the red wing is entirely governed by the 0\(^{\text{u}}\) state, the blue one by the 1\(_{\text{u}}\) state. Thus wing data can be quantitatively interpreted in a simple way in the frame of NNQST.

5.3.1 Red wing. — The red wing can be interpreted in term of a difference potential

\[
\Delta V_{0\text{u}} = V_{0\text{u}} - V_{0\text{u}} = \hbar \left( \frac{2 C_{3}}{r^{3}} - \frac{C_{6}^{0}}{r^{6}} \right)
\]

where the \(C_{12}^{0}\) term has been omitted, owing to the deep well of the 0\(^{\text{u}}\) curve at short internuclear distance. Then, taking into account the relative weight of the 0\(^{\text{u}}\) state, an analytical expression of \(k(v)\) is easily derived from eq. (7)

\[
k(v) = B \times \frac{16 \pi^{3}}{9} N^{2} v_{0} \frac{v_{0}}{v} \times \left\{ 1 + \left( \frac{C_{6}(v_{0} - v)}{C_{3}} \right)^{1/2} + \frac{C_{6}(v_{0} - v)}{C_{3}} \right\}. \tag{34}
\]

In figure 13 is plotted the evolution of \(k\) as a function of density at a fixed wavelength. The experimental values fit fairly well the quadratic law of eq. (34). The value of \(C_{3}\) is deduced from the \(f\)-value previously obtained from eq. (4). The Boltzmann factor \(B\) is derived from the ground state potential given by Barker et al. [76] (table III). Let us emphasize that only an estimation of \(C_{6}^{0}\) can be given: actually if the best fit is looked for by adjusting \(C_{6}^{0}\), it is realized that the method does not allow an accurate determination of this parameter. In fact, the alteration of the correspondence \(v \leftrightarrow r\) introduced by a change...
Fig. 13. — Index of absorption versus density of xenon at \( \lambda = 147.2 \) nm (red wing of 146.96 nm line). Triangles : reflectance data ; full curve : theoretical curve from eq. (34) with 

\[
C_3 = 4.26 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad \text{and} \quad C_6^0 = 10 \times 10^{-33} \text{ cm}^6 \text{ s}^{-1}.
\]

of \( C_6^0 \) is almost cancelled by the effect of the Boltzmann factor \( B \).

A similar behaviour is observed for the red wing of the krypton line associated to the \( 0^+ \) state, so that no improvement can be expected for the estimated potential of Barr et al. [102] (\( \epsilon \sim 8000 \) cm\(^{-1}\), \( r_e \sim 2.5 \) Å).

5.3.2 Blue wing. — From the preceding discussion we know that repulsive effects arise only from close interactions and, as a consequence of the criteria previously discussed, NNQST may be applied very close to the line centre. Then the blue wing can be interpreted in term of the difference potential \( \Delta V_1 \), (eq. (8bis)) where \( C_6^1 \) and \( C_12^1 \) are unknown.

We first tabulate all the couples \( (C_6^1, C_12^1) \) which yield \( \epsilon = -15 \) cm\(^{-1}\). The \( r_e \)-value associated with the minimum is determined by the conditions 

\[
\Delta V_1 (r_e) = \epsilon, \quad (d (\Delta V_1) / dr)_{r=r_e} = 0
\]

which gives

\[
r_e = \left[ \frac{3 C_3 - (9 C_3^2 - 32 C_6^1 \epsilon / h)^{1/2}}{8 \epsilon / h} \right]^{1/3}.
\]

Thus, to a value of \( C_6^0 \) there corresponds a value of \( r_e \) from which \( C_12^1 \) can be calculated.

Eq. (7) is then written as a function of \( r 

\[
k(r) = \frac{\hbar B q_e^2 N^2}{12 m e_0} \times \frac{2}{3} \times \frac{f}{v} \left| \frac{3 r^2}{d \Delta V(r)/dr} \right|
\]

and b). Each curve is fitted with a couple \( (C_6^1, C_12^1) \).

We then note that the fit is good only at the lower density and that the two couples giving the best fits differ by 15\% . This rather poor agreement may be corrected in an empirical way by taking into account the experimental shift \( v_0 \rightarrow v_0' \). Then the fit is obtained for almost identical values of \( C_6^1 \) and \( C_12^1 \) at low density whereas these values of \( C_6^1 \), \( C_12^1 \) give a much better fit at high density. The best couple is

\[
\begin{align*}
C_6^1 &= 12.0 \times 10^{-32} \text{ cm}^6 \text{ s}^{-1} \\
C_12^1 &= 10.5 \times 10^{-76} \text{ cm}^{12} \text{ s}^{-1}.
\end{align*}
\]

Figure 15 gives the results obtained for the 123.5 nm krypton blue wing with the values :

\[
\begin{align*}
C_6^1 &= 6 \times 10^{-32} \text{ cm}^6 \text{ s}^{-1} \\
C_12^1 &= 3 \times 10^{-76} \text{ cm}^{12} \text{ s}^{-1}.
\end{align*}
\]

From these values and the result of Barker et al. [76] for the ground state potentials, the potentials for the \( 1_u \) states are easily obtained.

All results are summarized in tables III and IV.
6. Conclusion. — We have reported results about line broadening, from high density measurements in xenon and krypton. Emphasis has been laid on the method which, combining normal incidence reflectance measurements and Kramers-Krönig analysis, is particularly well suited to this kind of study since it yields the whole profile. The method also appears as the only one adapted to the frequency range where many-body effects play a major part. Getting the whole profile is worth while since quantitative information is thus obtained for the integrated area and the evolution of the maximum of the index of absorption, allowing comparison with f-data or kM prediction. It also allows the study of the shift which thus has been ascribed to the effect of Van der Waals forces.

But, from a quantitative point of view, it is NNQST which provides the most interesting conclusions with regard to interatomic potential curves of the first excited states of Xe2 and Kr2. Especially the respective 1_u states are found to be slightly attractive allowing a definite conclusion about the origin of the blue molecular systems.

Therefore, we think that high density reflection measurements on gases or vapours constitute a valuable source of information. Especially, they provide data for the central part of the line, a region which cannot be yet interpreted by existing theories when both resonance and Van der Waals forces compete and we hope the method will stimulate theoretical work.

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References
[1] FUHR, J. R., WISE, W. L. and ROZSMAN, L. J., Bibliography on Atomic Line Shapes and Shifts, N.B.S. Special publication 366 (1972); suppl. 1 (1974); suppl. 2 (1975);