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High-density resonant shift of atomic lines of krypton and xenon in the wavelength range 118–150 nm*

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Absorption spectra of high-density pure krypton and xenon gases, in the wavelength range 118–150 nm and the density range 1–80 amagat, exhibit a red shift of all the atomic lines. The shifts are interpreted by taking into account the high-density interactions with the help of the local field correction of Lorentz introduced in classical dispersion theory.

I. INTRODUCTION

The density-induced modification of the atomic-gas absorption lines have been attracting considerable attention for a long time,[1] but in the particular case of resonant broadening studies, experimental and theoretical difficulties have generally limited the explored density range below 1 amagat.[1a]

A major theoretical difficulty arises from the necessity of taking into account the transfer of electronic excitation. The treatment is usually restricted to the binary collision approximation, which is only valid at low density. In this case most of theories reach the same conclusion: no shift and linear dependence of half-width with density is predicted, which is generally in agreement with experiments.[2] At higher densities, many-body resonant interactions are present. A complete treatment of the problem is therefore very difficult, and the various approaches[3–18] lead, when a conclusion is possible, to different results for the half-width (linear or nonlinear variation with density), or for the shift (red, blue, or null).

The lack of experimental results is a severe handicap to further theoretical development, but important experimental difficulties also arise in high-density atomic resonance broadening studies: (i) They are restricted to rare gases whose absorption lines lie in the far ultraviolet, or to metallic vapors, which imply study at high temperature. (ii) As the absorption coefficients are too large to allow transmission studies, line profiles are attainable only by selective reflection experiments.[19,20]

Nevertheless, we have shown that it is possible to measure the high-pressure shift of the absorption maximum, by using a specially designed cell.[21] The following paper presents the results obtained by this method, for xenon and krypton lines in the spectral range 118–150 nm at densities between 1 and 80 amagats.

II. EXPERIMENTAL

In our experiments, the variable length cell[21] is equipped with MgF_2 windows, and the convex plane has a radius of curvature equal to 0.25, 1.0, or 4.0 m.

The experimental setup is a conventional one: the background is the Baloffet-Romand-Vodar continuum[22] given by a vacuum spark; it is focused onto the spectrograph slit by a toroidal mirror. The cell is very close to the slit, for the method demands that the cell and the photographic film be optically conjugated. The vacuum spectrograph is equipped with a 1-m normal incidence concave grating, with 2000 grooves/mm giving a reciprocal dispersion of 0.5 nm/mm in the whole range. Calibration lines are given by an auxiliary low-pressure discharge source.[23]

Xenon and krypton gases (Air Liquide, N35 quality, impurity rate <0.05%) are used without further purification. The cell-filling device includes a sorption pump, a manometer and a thermocompressor. Experiments are performed at room temperature. The maximum pressure is 100 bars for krypton and 70 bars for xenon, corresponding to densities of 110 and 260 amagats, respectively. The krypton densities versus pressure are taken from the paper of Trappeniers *et al.*[24] and those of xenon are calculated with the equation of state given by Beattie *et al.*[25]

Figure 1 reproduces part of the xenon spectrum. The shifts of the absorption maxima are measured on microphotometer records.

III. RESULTS

The method used does not provide a line profile but gives interesting qualitative information about relative intensities of molecular absorption previously observed only at low density.[26–28] The in-

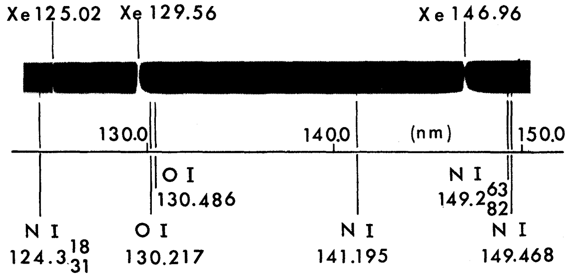

FIG. 1. Xenon spectrum at $p = 7$ bar, $t = 19\,°\mathrm{C}$; NI and OI are calibration lines obtained by a low-pressure discharge.

crease in density favors the pair formation, so that the important growth of molecular absorption restricts the density range of results for all lines.

A. 123.58-nm krypton line

The molecular systems associated with this line have been reported at very low pressure by Tanaka.[28] We observe that the red system remains the most intense with increasing density. The absorption on both the red and blue sides of the atomic line increases so rapidly in our density range, that, at about 80 amagats, it becomes comparable with that of the atomic line. As the density continues to increase beyond this point, an overlapping takes place so that the measurement is no longer meaningful for the atomic line. Thus the curve giving the shift versus density (Fig. 2) must be limited to 80 amagats.

The weak red structure, which Tanaka observed at 125.12 nm and called "spectral demarcation," begins to appear on our spectra at 15 amagats. Its relative intensity remains weak, and thus could not be observed in the reflection spectra.[19]

The 116.49-nm krypton line has not been studied, since it is too close to the transparency limit of the cell windows.

B. 146.96-nm xenon line

The behavior of the absorption spectrum of xenon near the 146.96-nm line is similar to that of the 123.58-nm krypton line.

The curve of Fig. 3 gives the shift of the atomic absorption maximum versus density up to 50 amagats. Actually, even at 30 amagats, the red system observed by Castex and Damany[26] has enough intensity to alter the profile, and thus the shift measurement becomes less accurate. The absorption band near 149.3 mm mentioned by Tanaka[28] appears at approximately the same density; it is analogous to the weak krypton band seen above.

C. 129.56-nm xenon line

The broad red and the narrow blue molecular system observed in the low-pressure spectra,[26] increase with comparable relative intensities and begin to disturb the measured shift of the atomic line when the density reaches 35 amagats. Indeed, it can be seen on Fig. 4 that, at that density, there is a quick change in the shift, and thus the measurement at higher densities cannot be strictly assigned to the atomic line.

D. 125.02- and 119.20-nm xenon lines

Analogous features are also observed for these two lines. Figures 5 and 6 give the observed shifts. For the same reason as above, the results of the atomic line shift are significant only below 25 amagats.

It has not been possible to study the 117.04-nm xenon line because of spectral limitations.

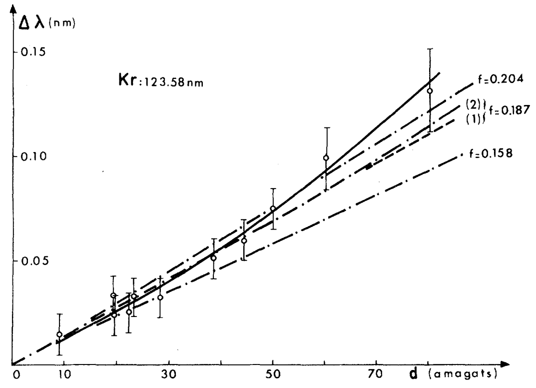

FIG. 2. Shift of the absorption maximum of the 123.58-nm krypton line. Full curve: our experimental data; dashed curves: calculated shift for three different oscillator strength values; in the case $f = 0.187$ results are given from Eqs. (1) and (2) as an illustration.

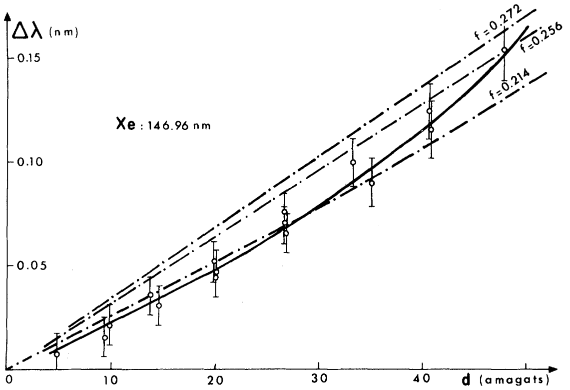

FIG. 3. Shift of the absorption maximum of the 146.96-nm xenon line. Full curve: our experimental data; dashed curves: calculated shift values.

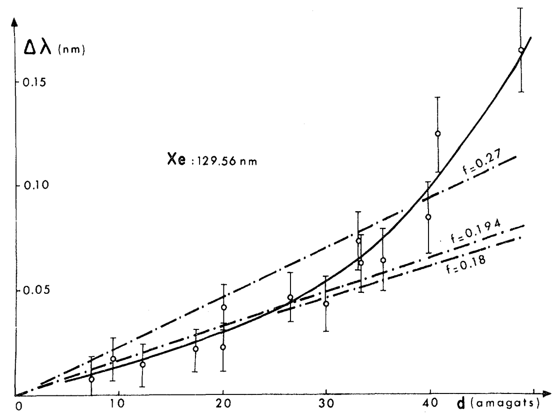

FIG. 4. Shift of the absorption maximum of the 129.56-nm xenon line. Full curve: our experimental data; dashed curves: calculated shift values.

IV. SHIFT MEASUREMENT ACCURACY

Three factors of uncertainty are present.

(i) The first comes from the measurement of the transmission minimum wavelength. At low density the corresponding accuracy is ±0.01 nm, and is only due to the spectrograph resolving power. At higher densities the error increases progressively as the line broadens. The accuracy is thus dependent on the line and can decrease to ±0.02 nm as can be seen in Figs. 2–6.

(ii) The uncertainty that could arise from the progressive overlapping of the atomic lines by the molecular bands can be disregarded in the limited density range where results are given.

(iii) The third factor that could limit the accuracy is the selective reflection that occurs at the boundary of the solid-gas dioptre.[19] It is well known that the wavelength of the reflectance maximum is shorter than the wavelength of the corresponding absorption maximum. As all the shifts we have measured are towards long wavelengths, the existence of a selective reflection can only lead to a systematic underevaluation of the true shift.

The corresponding correction can be calculated with the help of our previous results on selective reflection, but this calculation is not exact for two reasons: (a) The method used here does not supply a true profile of the spectral line. (b) Owing to the extremely short length of the cell, we cannot assume that the selective reflection takes place completely and independently at each magnesium fluoride-gas dioptre; thus, taking into account two independent selective reflections in the calculation, we have overestimated the correction.

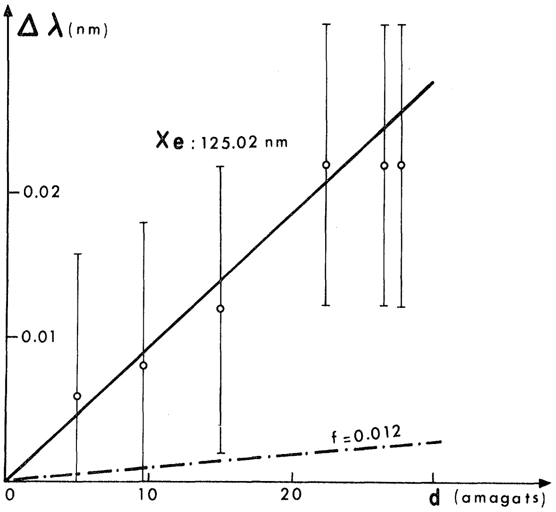

FIG. 5. Shift of the absorption maximum of the 125.02-nm xenon line. Full curve: our experimental data; dashed curve: calculated shift.

If one considers the 146.96-nm line in the least favorable conditions, i.e., at a density of 15 amagats where the reflectance is at a maximum,[19] the correction is +0.007 nm, which is smaller than other errors.

V. CALCULATION OF SHIFT

In the case of high densities, the treatment of resonance interactions is an enormous task and, apart from the work of Lorentz[3] carried on by Weisskopf,[6] no calculation of the shift seems to remain valid. Thus we shall now only consider

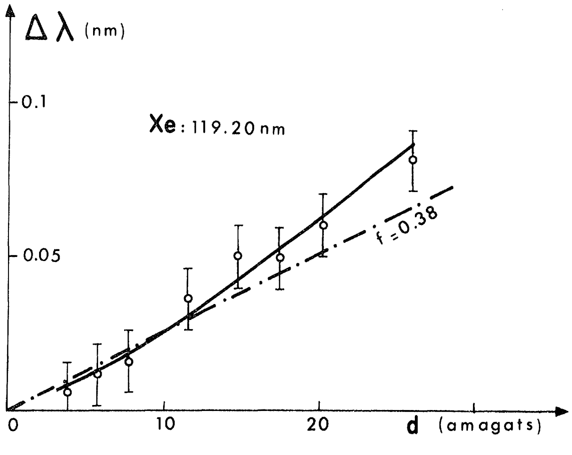

FIG. 6. Shift of the absorption maximum of the 119.20-nm xenon line. Full curve: our experimental data; dashed curve: calculated shift.

this contribution to the resonant shift although other causes may be present.[17]

In Lorentz approach, many-body effects are taken into account as a whole by introducing his well-known local field correction in the framework of the classical dispersion theory.[29] Neglecting any contribution to the refractive index from other resonances, i.e., taking the refractive index n equal to one far-from-resonance frequency ω_0, Lorentz found that the shift is given by[30]

$$\omega_0'^2 = \omega_0^2 - Nfq_e^2/3m\epsilon_0 \tag{1}$$

(MKSA units). Here ω_0 and ω_0' are, respectively, the unshifted and the shifted angular frequency; N is the atom density; f is the oscillator strength of the transition; and m and q_e are, respectively, the electron mass and charge.

Lorentz's assumption, $n = 1$ far from ω_0, is no longer valid at high density, especially if other resonances are present not too far from ω_0. Let $n'(\omega)$ be their contribution (real) to the refractive index. A straightforward calculation gives

$$\omega_0'^2 = \omega_0^2 - \frac{Nfq_e^2}{3m\epsilon_0}\left(\frac{n_0^2+2}{3}\right), \tag{2}$$

where $n_0 = n'(\omega_0)$. If $n_0 = 1$, which is the case considered by Lorentz, Eq. (2) reduces to Eq. (1).

As $\omega_0' \sim \omega_0$, we shall use the result in the form

$$\begin{aligned}\Delta\lambda &= \frac{\lambda_0^3}{8\pi^2c^2}\,\frac{Nfq_e^2}{3m\epsilon_0}\left(\frac{n_0^2+2}{3}\right)\\ &= 1.494\times10^{-16}\lambda_0^3Nf\left(\frac{n_0^2+2}{3}\right),\end{aligned} \tag{3}$$

where c is the speed of light. It should be noted that Eqs. (1)–(3) concern the shift of $\mathrm{n}\kappa$, the product of the real and imaginary parts of the complex refractive index ($n = \mathrm{n} - i\kappa$, $\kappa = kc/2\omega$, k being the absorption coefficient).

The shift of $\kappa_{\max}$, which corresponds to our observations, is equal to that of $\mathrm{n}\kappa$ only at low densities. At higher densities the shift does not have a simple analytical expression, and the correction to be introduced depends on the damping constant γ of the resonance.[31] As γ is not determined in this work we cannot calculate this correction, which should lower the shift derived from Eqs. (1)–(3).

The work already published on oscillator strengths[32–45] for the considered lines is summarized in Table I. Figures 2–6 give the shifts calculated from some of these values.

To evaluate the term $(n_0^2+2)/3$ of Eq. (2), and Eq. (3), we have used the dispersion equation given by Chaschina and Schreider[46] and calculated the high-density index of refraction by means of the Lorentz-Lorenz formula. That correction is weak in our density range, as illustrated in Fig. 2.

Apart from the case of the 125.02-nm line of xenon, whose oscillator strength is one order of magnitude less than the others, the present calculation takes into account the observed shifts. Moreover, the correction that comes from the refractive index, although weak, bends the calculated curve in the direction of the experimental curvature. Thus we think that the shift given by Lorentz plays a leading part in the whole reso-

TABLE I. Oscillator strengths of the resonance lines of krypton and xenon as determined by various investigators.

Reference	Kr 123.58 nm	Xe 146.96 nm	Xe 129.56 nm	Xe 125.02 nm	Xe 119.22 nm
		Experimental			
Ref. 32	0.266	...	...	...	...
Ref. 33	...	0.256	0.238	...	...
Ref. 34	0.166	...	...	...	...
Ref. 35	0.158	0.26	0.27	...	...
Ref. 36	0.21	0.28	0.23	...	...
Ref. 37	0.204	...	...	...	...
Ref. 38	0.187	...	0.194	...	...
Refs. 39 and 40	0.173	0.26	0.19	0.0095	0.395
Ref. 41	...	0.214	0.180	...	...
Ref. 42	...	0.272	0.189	0.012	0.381
		Theoretical			
Ref. 43	0.138	0.194	0.147	...	...
	0.152	0.190	0.170	...	...
Ref. 44	0.2	0.28	0.25	...	...
Ref. 45	0.176	0.246	0.268	...	...
	0.193	0.251	0.230	...	...

nant shift.

For the 125.02-nm line, the observed shift is much larger than the calculated one. We do not think that the neighboring red line is responsible for so large an effect, since we have limited the range of our results. A more fundamental reason must therefore be found for this discrepancy.

VI. CONCLUSION

This work, performed in the vacuum uv on rare gases by means of a suitable cell, would seem to be the first example of the direct observation of the shift of atomic resonance lines.

The sign and magnitude of the observed shifts are in reasonable agreement with Lorentz theory, which we adapted to the case of high densities. It is worthy of note that this simple theory predicts a magnitude of the shift connected with the oscillator strength; this is well illustrated by the behavior of the various lines of xenon.

We hope that our experimental results will stimulate new investigations, in particular theoretical ones, in the field of high-density resonant interactions.

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[1] J. R. Fuhr, W. L. Wiese, and L. J. Roszman, *Bibliography on Atomic Line Shapes and Shifts*, N. B. S. Special Publication 366 (U. S. Department of Commerce, Washington, D. C., 1972); and 366 Suppl. I (1974).

[1a] In this case of xenon the amagat density unit (1 amagat) corresponds to 4.4927×10^{-5} mole cm^{-3}, i.e., also to 27.067×10^{18} atoms cm^{-3} [from A. Michels, T. Wassenaar, and P. Louverse, Physica 20, 99 (1954)]. In the case of krypton, 1 amagat $\equiv 4.4738\times10^{-5}$ mole cm^{-3} $\equiv 26.953\times10^{18}$ atoms cm^{-3} (Ref. 24). For a general definition of the amagat unit, see, for instance, H. G. Jerrard and D. B. McNeill, *A Dictionary of Scientific Units* (Chapman and Hall, London, 1964), 2nd ed.

[2] For a bibliography on this subject see, for instance, P. R. Berman and W. E. Lamb, Phys. Rev. 187, 221 (1969); and D. Perrin-Lagarde and R. Lennuier, J. Phys. (Paris) 36, 357 (1975).

[3] H. A. Lorentz, Proc. R. Acad. Amst. 8, 591 (1906); see also H. A. Lorentz, *The Theory of Electrons* (Dover, New York, 1952), 2nd ed.

[4] J. Holtsmark, Z. Phys. 34, 722 (1925).

[5] J. Frenkel, Z. Phys. 59, 198 (1930).

[6] V. Weisskopf, Phys. Z. 34, 1 (1933).

[7] For 4, 5, and 6, see also, R. G. Breene, *The Shift and Shape of Spectral Lines* (Pergamon, New York, 1961), p. 194.

[8] U. Fano, Phys. Rev. 131, 259 (1963).

[9] G. P. Reck, H. Takebe, and C. A. Mead, Phys. Rev. 137, A683 (1965).

[10] D. W. Ross, Ann. Phys. (N.Y.) 36, 458 (1966).

[11] B. Bezzerides, J. Quant. Spectrosc. Radiat. Transfer 7, 353 (1967).

[12] B. Bezzerides, Phys. Rev. 159, 3 (1967).

[13] H. R. Zaidi, Phys. Rev. 173, 123 (1968).

[14] A. Ben-Reuven, in *Advances in Atomic and Molecular Physics*, edited by D. R. Bates and I. Esterman (Academic, New York, 1969), Vol. 5, p. 228.

[15] A. Ben-Reuven, Phys. Rev. A 4, 2115 (1971).

[16] C. A. Mead, Phys. Rev. A 5, 1957 (1972).

[17] R. Freidberg, S. R. Hartmann, and J. T. Manassah, Phys. Rep. 7, 102 (1973).

[18] F. Hynne, J. Quant. Spectrosc. Radiat. Transfer 14, 437 (1974).

[19] P. Laporte, Physica 79B, 276 (1975).

[20] P. Laporte and A. Leycuras, Rev. Phys. Appl. 7, 193 (1972).

[21] P. Laporte, Rev. Sci. Instrum. 45, 77 (1974).

[22] H. Damany, J. Y. Roncin, and N. Damany-Astoin, Appl. Opt. 5, 297 (1966).

[23] H. Damany, Licence Anvar. Manufactured by Creusot Loire (France).

[24] N. J. Trappeniers, T. Wassenaar, and G. J. Wolkers, Physica 32, 1503 (1966).

[25] J. A. Beattie, R. J. Barriault, and J. S. Brierley, J. Chem. Phys. 19, 1219 (1951).

[26] M. C. Castex and N. Damany, Chem. Phys. Lett. 13, 158 (1972); 24, 437 (1974).

[27] M. C. Castex, Chem. Phys. 5, 448 (1974).

[28] Y. Tanaka, K. Yoshino, and D. E. Freeman, J. Chem. Phys. 59, 5160 (1973).

[29] For this reason the shift given by Eq. (1) is called Lorentz shift.

[30] See also, F. Seitz, *Modern Theory of Solids* (McGraw-Hill, New York, 1940), p. 658; and R. W. Ditchburn, *Light* (Blackie, London, 1963), p. 565.

[31] R. Friedberg and S. R. Hartmann, Phys. Lett. 40A, 395 (1972).

[32] J. Koch, K. Fysiogr. Saellsk. Lund. Foerh. 19, 173 (1949).

[33] D. K. Anderson, Phys. Rev. 137, A21 (1965).

[34] R. Turner, Phys. Rev. 140, A426 (1965).

[35] P. G. Wilkinson, J. Quant. Spectrosc. Radiat. Transfer 5, 503 (1965); 6, 823 (1966).

[36] G. I. Chaschina and E. Ya. Schreider, Opt. Spectrosc. 20, 283 (1966); 22, 284 (1967).

[37] J. M. Vaughan, Phys. Rev. 166, 13 (1968).

[38] P. M. Griffin and J. W. Hutcherson, J. Opt. Soc. Am. 59, 1607 (1969).

[39] J. Geiger, Phys. Lett. 33A, 351 (1970).

[40] J. Geiger, in *Proceedings of the Fourth International Conference on V. U. V. Radiation Physics, Hamburg, July 1974* (Pergamon, Vieweg, 1975), p. 28.

[41] W. Wieme and P. Mortier, Physica 65, 198 (1973).

[42] Values given by K. T. Lu, Phys. Rev. A 4, 579 (1971), from the experimental results of S. Natali, C. E. Kuyatt, and S. R. Mielczarek (unpublished).

[43] J. Dow and R. S. Knox, Phys. Rev. 152, A51 (1966).

[44] P. F. Gruzdev, Opt. Spectrosc. 22, 170 (1967).

[45] M. Aymar, Physica 57, 178 (1972).

[46] G. I. Chaschina and E. Ya. Schreider, Opt. Spectrosc. 27, 79 (1969).