SOME REMARKS ON PRESSURE EFFECTS ON $2p^5 3p$–$2p^5 ns$ ($n = 5,\ 6,\ 7$) TRANSITIONS IN NEON

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The collisional broadening and shift of 494.5 nm spectral line of neon arising from $2p^5 3p$–$2p^5 7s$ transition, emitted from a low-pressure glow discharge in pure neon and neon–helium mixtures have been measured. The values of pressure broadening and shift coefficients were determined. Experimental data of 494.5 nm line as well as our earlier results for spectral lines originating from the $2p^5 3p$–$2p^5 ns$ ($n = 5,\ 6$) transitions are compared with those resulting from the Kaulakys and Ueda theories of pressure effects on Rydberg states.

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1. Introduction

The study of pressure broadening and shift of spectral lines is a valuable source of information about interaction between the excited and the ground state atoms and thus can verify the existing models of the interatomic potentials. In the previous papers from this laboratory the results of experiments concerning the pressure effects on spectral lines of neon arising from the transitions between configurations: $2p^5 3p$–$2p^5 nd$ ($n = 4$ [1], $n = 5,\ 6$ [2]), $2p^5 3s$–$2p^5 3p$ ($\lambda = 540$ nm [3]), $2p^5 3p$–$2p^5 ns$ ($n = 5$ [4], $n = 6$ [5]) were reported. Since there have been no experimental data on the influence of collisions on the neon states with $n = 7$ in the present investigation we have measured the profiles of the 494.5 nm Ne line which arises from the transitions between the $2p^5 7s$ and $2p^5 3p$ configurations. The main purpose of this work is to establish the values of the pressure broadening (β) and shift (δ) coefficients of this line at low density of perturbing atoms where the impact approximation is fully applicable. Upper states of neon spectral lines studied in the present work are excited highly enough to be treated as quasi-Rydberg states. For this reason an attempt is made in this paper to interpret the measured data obtained during the course of the present experiment for the 494.5 nm line as well as in our previous investigation for the $2p^5 3p$–$2p^5 ns$ ($n = 5,\ 6$) transitions on the basis of the theory of collision effects on optical lines involving Rydberg states [6, 7].

2. Experimental and data analysis

The neon lines were formed in emission in a glow discharge source. This source was identical to that described elsewhere [8] and consisted of a water-cooled glow discharge tube. In our experiments the cooling temperature was always kept constant at 298 K. Light was collected from the positive column of the low current (1.5 mA) glow discharge run at pressure in the range of 0.4–6.3 torr.

In a previous paper [2] we have measured the broadening and shift of the 486.3 nm Ne line ($2p^5 3p$–$2p^5 6d$) as a function of the discharge current. We have found that for glow discharge the Stark broadening of the 486.3 nm Ne line is completely negligible for discharge currents below 1.8 mA. It should be noted that the upper level ($2p^5 6d$) of the 486.3 nm Ne line corresponds to the effective quantum number $n^\star = 5.99$. For the 494.5 nm Ne line analysed in the present experiment the effective quantum number of the upper state ($2p^5 7s$) equals 5.68 so it is lower than that for the 486.3 nm line. One can thus conclude that the influence of Stark effects on the profile of the 494.5 nm line can be neglected and the broadening and shift data should mainly reflect the effects of interaction between the emitting neon atom and perturbing neutral particles (Ne or He) and not charged particles.

Line profiles were analysed using a pressure-scanned Fabry–Perot etalon of the type described by Bielski et al. [9] with dielectric coating and a 1.513 cm spacer (free spectral range 0.3305 cm^{-1}). Measurements of the pressure shift of the line centre were made relative to the same line formed in an electrodeless RF neon discharge tube and maintained under constant conditions. The pressure of neon in the reference source was kept at 0.4 torr. The intensity distribution in a broadened line was registered using a photomultiplier in the photon counting mode.

Accurate tests performed for many spectral lines studied in this laboratory have shown that at low densities the line shapes $I(\nu)$ obtained by means of our Fabry–Perot interferometer can be fitted very well to an analytic formula obtained by Ballik [10],which is the convolution of the instrumental profile of the ideal Fabry–Perot etalon and the Voigt profile. In the present study measurements of line shapes were performed using the natural neon which is the mixture of ^{20}Ne (90.92%), ^{21}Ne (0.257%) and ^{22}Ne (8.823%) isotopes. In a good approximation the contribution of the ^{21}Ne isotope to the observed intensity can be omitted so that the resultant line shape is the superposition of two isotope components. Assuming that the pressure broadening and the shift of both components are the same and using the Ballik [10] formula the resultant line shape $I(\nu)$ is given by (cf. Bielski et al. [4]):

$$I(\nu) = A \sum_{k=1}^{2} \alpha_k \left\{ 0.5 + \sum_{m=1}^{\infty} (\mathrm{Re}^{-L})^m \exp(-0.25 D^2 m^2) \right.$$
$$\left. \times \cos m \frac{2\pi}{\Delta\nu_{\mathrm{i}}} [(\nu - \nu_0) + d_k - \Delta] \right\}, \qquad (1)$$

where A is a normalizing factor independent of the wave number ν. Here R is the reflection coefficient of the etalon plates, $L = (\pi\gamma_L)/(\Delta\nu_i)$, $D = (\pi\gamma_G)/(\Delta\nu_i\sqrt{\ln 2})$, $\Delta\nu_i$ — the free spectral range of the interferometer, ν_0 — the unperturbed wave number of the line, d_k — isotope shift of the weaker component relative to the stronger component, α_k — relative intensity of the k-th component of a line ($\sum \alpha_k = 1$), γ_L and γ_G — half-widths of the Lorentzian and Gaussian components of the measured profile, respectively, and Δ — pressure shift of the stronger component of the line.

In the previous work done in this laboratory [2] Eq. (1) was used to determine the values of γ_L and γ_G of the Lorentzian and Gaussian half-width of neon spectral lines, the pressure shift Δ of their maxima as well as the values d_k of the isotope shift. These parameters were determined by a least-square fit of the measured interferograms at various perturbing gas densities to Eq. (1) using an algorithm given by Marquardt [11]. Using a best-fit procedure we found for the isotope shift of this line the value $(43.0 \pm 2.0) \times 10^{-3}$ cm^{-1}.

3. Results and discussion

Figure 1 shows the plots of the Gaussian half-widths γ_G of the 494.5 nm Ne line against the pressure of the perturbing gas in the glow discharge tube. As it can be seen for the two perturbing gases (He, Ne) the Gaussian half-width of this line is practically independent of the pressure.

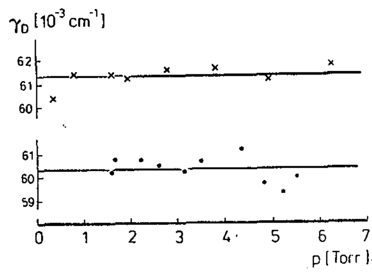


Fig. 1. Plots of the Gaussian half-width γ_G for the 494.5 nm neon line against perturbing gas pressure. Experimental points: × — Ne*–He interaction, • — Ne*–Ne interaction.

We should emphasize that in the case of our Fabry–Perot interferometer the instrumental contribution to the resultant Gaussian half-width γ_G is negligible so that γ_G can be fully identified with the Doppler half-width γ_D due to the thermal motion of the emitting atoms. The lack of the dependence of the Gaussian half-width on the gas pressure may be regarded as an evidence that the pressure broadening of the line under investigation is statistically independent of the Doppler broadening (cf. Ward et al. [12]). We can thus conclude that for this line the velocity changing collisions do not play any essential role.

The average Doppler half-widths $\overline{\gamma_D}$ determined from the plots shown in Fig. 1 and corresponding average Doppler temperatures are listed in Table I. Using the average Doppler temperatures and the measured values of the gas pressure we can find the density N of the perturbing gases.

TABLE I

The average Doppler half-width $\overline{\gamma_D}$ and temperature $\overline{T_D}$. Numbers in parentheses represent standard deviation.

λ [nm]	494.5	
perturber	He	Ne
$\overline{\gamma_D}$ [10^{-3} cm^{-1}]	61.3 (1.2)	60.3 (1.4)
$\overline{T_D}$ [K]	359 (6)	343 (12)

Figure 2 shows the plots of the Lorentzian half-width γ_L of the 494.5 nm Ne line, perturbed by neon (Ne*–Ne interaction) and helium (Ne*–He interaction) against the perturbing gas density N. As can be seen the Lorentzian half-width

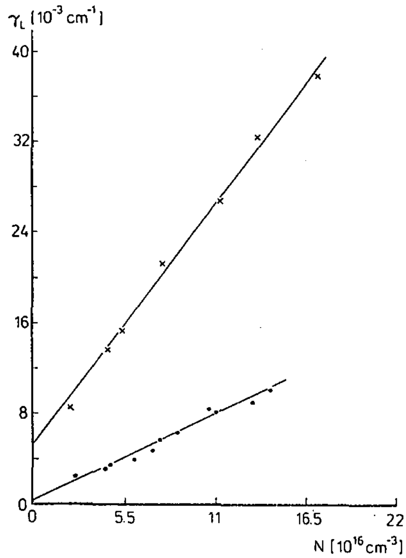


Fig. 2. Plots of the Lorentzian half-width γ_L for the 494.5 nm neon line against perturbing gas density N. Experimental points: × — Ne*–He interaction, • — Ne*–Ne interaction.

depends linearly on the density

$$\gamma_L = \gamma_L^{(0)} + \beta N, \tag{2}$$

where β is the pressure broadening coefficient and $\gamma_L^{(0)}$ denotes the "residual" half-width which for ideal Fabry–Perot interferometer should, in principle, correspond to the natural line width. It should be noted, howewer, that in the case of real interferometer $\gamma_L^{(0)}$ may contain some instrumental contribution. The plots of the shift Δ of the 494.5 nm Ne line against the perturbing gas density as shown in Fig. 3 can also be described by the linear relation

$$\Delta = \Delta^{(0)} + \delta N, \tag{3}$$

where δ is the pressure shift coefficient and $\Delta^{(0)}$ denotes the "residual" value of the pressure shift which comprises the shift of the line in the reference source and that resulting from the numerical data analysis.

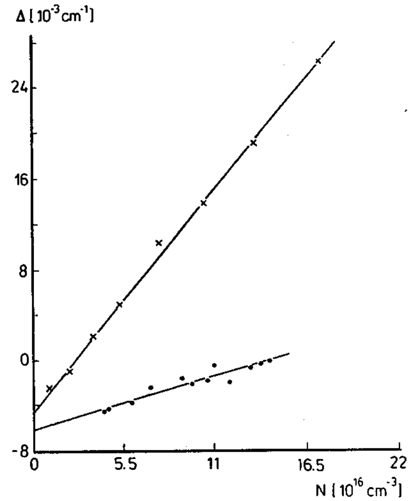


Fig. 3. Plots of the shift Δ for the 494.5 nm neon line againts perturbing gas density N. Experimental points: × — Ne*–He interaction, o — Ne*–Ne interaction.

For real, i.e. non-ideal, Fabry–Perot interferometer the residual values of $\gamma_L^{(0)}$ and $\Delta^{(0)}$ can be connected to imperfections of etalon plates and uncertainties in the isotope shift determination.

Since in the present study we are dealing with the broadening and shift coefficients β and δ only and not with the absolute values of γ_L and Δ the residual values of $\gamma_L^{(0)}$ and $\Delta^{(0)}$ will not be discussed here.

The values of β and δ coefficients determined by the least-square fit to linear relations (2) and (3) for Ne*–He and Ne*–Ne interactions are listed in Tables II and III, respectively. Let us note that for both Ne*–He and Ne*–Ne the positive values of δ coefficient were observed ($\delta > 0$).

It is important to note that the value of the ratio δ/β for both Ne*–Ne and Ne*–He interactions are greater than the limiting upper value 0.15, resulting from the impact theory for the Lennard–Jones potential (cf. [5]). This result indicates that the Lennard–Jones potential is inadequate for the description of collisional

TABLE II

Experimental (Exp.) and theoretical (T_1 — Kaulakys [7], T_2 — Ueda [6]) values of the pressure broadening (β) and shift (δ) coefficients (in units 10^{-20} cm^{-1}/atom cm^{-3}) for 494.5 nm Ne line, for $Ne^{\star}$–He interactions. Numbers in parentheses represent standard deviation. $n^{\star}$ — effective quantum number.

λ [nm]	494.5		
$n^{\star}$	5.684		
	β	δ	δ/β
Exp.	19.49 (0.65)	17.70 (0.34)	0.91 (0.05)
T_1	18.11	18.34	1.01
T_2	18.94	–	–

TABLE III

Experimental (Exp.) and theoretical (T_1 — Kaulakys [7], T_2 — Ueda [6]) values of the pressure broadening (β) and shift (δ) coefficients (in units 10^{-20} cm^{-1}/atom cm^{-3}) for 494.5 nm Ne line, for $Ne^{\star}$–Ne interactions. Numbers in parentheses represent standard deviation. $n^{\star}$ — effective quantum number.

λ [nm]	494.5		
$n^{\star}$	5.684		
	β	δ	δ/β
Exp.	6.65 (0.69)	4.17 (0.55)	0.63 (0.15)
T_1	4.00	2.47	0.62
T_2	3.69	–	–

effects on the 494.5 nm neon spectral line.

For this spectral line of neon its upper state ($3p^5 7s$) is excited highly enough to be considered in rough approximation as nearly Rydberg one. Analytical expressions for the pressure broadening coefficients for optical lines involving Rydberg levels have recently been derived by Kaulakys [7] and Ueda [6] in the framework of the impact approximation. Kaulakys [7] has also given expressions for the pressure shift coefficients for such spectral lines. Both the Kaulakys [7] and Ueda

[6] treatments employ the "free electron" model due to Fermi [13] in which the interaction between a Rydberg atom and a perturber is described in terms of the interactions between a nearly free electron and the perturber. The broadening and shift coefficients are then expressed by means of the scattering length L and the polarizability α of the perturbing atom as well as the effective quantum number $n^\star$ of the Rydberg level and the mean relative velocity $\bar{v}$ of the interacting atoms. The values of the broadening coefficient (β) calculated from the Kaulakys [7] and Ueda [6] treatments as well as the shift coefficients (δ) computed from a formula derived by Kaulakys [7] are listed in Tables II and III where they are compared with our experimental data. In these calculations we used the experimental values of the scattering length $L = 1.15$ a.u. for He and $L = 0.2$ a.u. for Ne reported by Golovanivsky et al. [14]. The conditions of applicability of the Kaulakys and Ueda treatments for the $2p^5 7s$ states for both Ne*–Ne and Ne*–He interactions, have the form

$$n^\star > 0.7\left(|L|\alpha^{-1/6}v^{-5/6}\right)^{1/3}. \quad (4)$$

Here $n^\star$ is the effective quantum number of the upper level.

For the 494.5 nm Ne line arising from the transition $2p^5 3p$–$2p^5 7s$ studied in the present work this condition is fulfilled. As can be seen from Table II for Ne*–He interactions the broadening (β) and shift (δ) coefficients calculated from these treatments are in good agreement with our experimental data. Contrary to that in pure neon (Ne*–Ne) the experimental values of both broadening (β) and shift (δ) coefficients are greater by a factor of 1.7 than the theoretical ones.

In order to present the overall dependence of the line profile parameters on $n^\star$ for all neon spectral lines arising from the $2p^5 3p$–$2p^5 ns$ ($n = 5$–7) transitions in neon we have calculated the β- and δ-coefficients using the Kaulakys–Ueda treatments and compared them with experimental values determined in this laboratory [4, 5]. Results of these comparisons are shown in Figures 4–7.

As can be seen from Fig. 4 in the case of perturbation by helium the theoretical broadening coefficients agree well with experimental data. Figure 5 shows that for the shift coefficients the theoretical values agree well with experiment for the lines originating from the $2p^5 6s$ ($n^\star = 4.69$) and the $2p^5 7s$ ($n^\star = 5.68$) states. In the case of the $2p^5 3p$–$2p^5 5s$ transitions in neon perturbed by helium the validity conditions of the Kaulakys formula for the shift are not fulfilled. For this reason we are unable to compare our experimental shift coefficient for these lines, determined in a previous work [4], with theory. Figure 6 shows that in the case of self-broadened neon lines (Ne*–Ne) the experimental values of the β-coefficients are greater by a factor of 1.7 than those calculated from the Kaulakys treatment.

In Fig. 7 we have presented the comparison of theoretical pressure shift coefficients (δ) computed from the Kaulakys formula with the experimental shift data for pure neon (Ne*–Ne) determined in this laboratory. We can see again that our experimental shift coefficients disagree with theory except the lines originating from the $2p^5 6s$ state ($n^\star = 4.69$) where the agreement although poor seems to be reasonable. For the 494.5 nm line corresponding to the $2p^5 7s$ state the experimental shift coefficient is 1.7 times greater than the theoretical value. Contrary to that for the lines originating from the $2p^5 5s$ states the experimental shift coefficient is

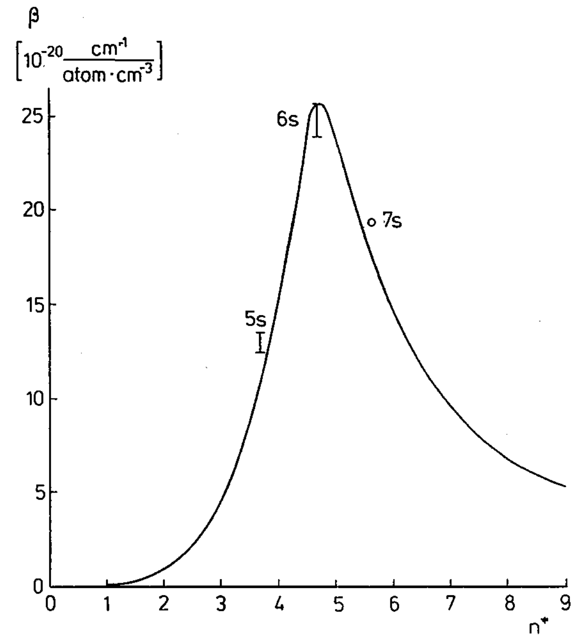


Fig. 4. Plots of the β-coefficients determined for neon spectral lines arising from the $2p^5 3p$–$2p^5 ns$ ($n = 5$–7) transitions perturbed by helium as a function of effective quantum number $n^\star$ of the upper state. Vertical bars determine the range of the experimental β-values.

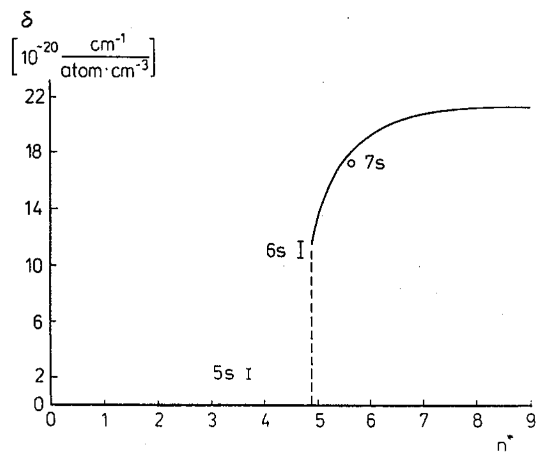
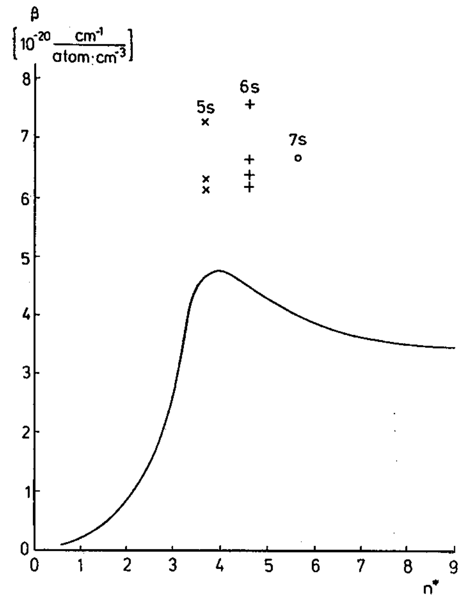


Fig. 5. Plots of the δ-coefficients determined for neon spectral lines arising from the $2p^5 3p$–$2p^5 ns$ ($n = 5$–7) transitions perturbed by helium as a function of effective quantum number $n^\star$ of the upper state. Vertical bars determine the range of the experimental δ-values.



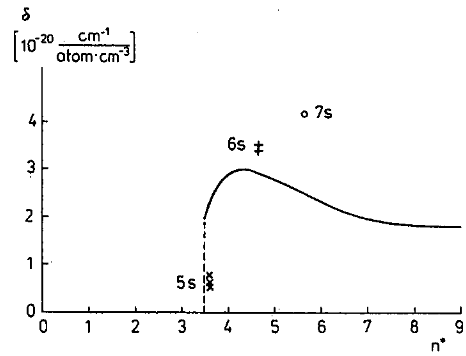


Fig. 6. Plots of the β-coefficients determined for neon spectral lines arising from the $2p^5 3p$–$2p^5 ns$ ($n = 5$–7) transitions perturbed by neon as a function of effective quantum number n^* of the upper state. ×, +, ∘ — experimental points.

Fig. 7. Plots of the δ-coefficients determined for neon spectral lines arising from the $2p^5 3p$–$2p^5 ns$ ($n = 5$–7) transitions perturbed by neon as a function of effective quantum number n^* of the upper state. ×, +, ∘ — experimental points.

three times smaller than that resulting from the Kaulakys theory.

4. Concluding remarks

We have shown that the Kaulakys–Ueda treatment can adequatly deal with collision effect induced by helium ground state atoms on spectral lines of neon arising from the $2p^5 3p$–$2p^5 ns$ transitions (with $n = 5$–7). On the other hand, however, we have also shown that this treatment fails in case of perturbation of the same Ne spectral lines by ground state neon atoms. The correct interpretation of the broadening and shift in the case of Ne*–Ne interactions clearly requires a more elaborate treatment.

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