Krypton influence on the spectral line shape of Cd 326.1 nm

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Abstract. The line center of the Cd intercombination spectral line 326.1 nm (51S0 → 53P1) perturbed by Kr has been investigated using a high - resolution scanning Fabry-Perot interferometer. The van der Waals and Lennard –Jones potentials for Cd-Kr system has been calculated using the Coulomb approximation. The values of the pressure broadening (β) and shift (δ) coefficients for the studied line at temperature 468 K, density of cadmium N = 4.02 10^{12} cm^{-3} and gas Kr pressure ranged from 3 to 95 Torr has been obtained and compared with theoretical and experimental published values.

1. Introduction
Spectral line shape analysis is a powerful diagnostic tool for many media in extreme conditions of temperature and pressure. Measurements of the pressure broadening and shift of atomic spectral lines of van der Waals molecules are an important source of information about the interaction potentials between radiating and perturbing atoms. In the molecular state model the results are sensitive to the interaction potential, particularly in the region of long range interaction.

During the past several decades, there have been numerous investigations of van der Waals molecules especially for pure cadmium and cadmium inert gas systems [1-20]. There are some experimental and theoretical papers [10-20] that have been performed for obtaining the interatomic potentials for Cd + Kr using Cd intercombination spectral line at 326.1 nm (5^3P_1 → 5^1S_0).

In the present paper the measurements of the width and shift of the natural Cd intercombination spectral line at 326.1 nm (5^1S_0 → 5^3P_1) perturbed by Kr at low pressures are carried out. The broadening and shift coefficients β and δ for Cd line have been obtained experimentally and theoretical using the Coulomb Approximation (CA) for van der Waals and Lennard – Jones potentials . Also, in this work an attempt was undertaken to verify these potential curves obtained by different experimental and theoretical methods [10-20] using the pressure broadening and shift coefficients (β and δ) of the same spectral Line perturbed by Kr using the classical theory of Lindholm [21] and Foley [22].

2. Experimental part

2.1. Experimental set-up
The measurements were made with the aid of a spectrometer with electrically tunable scanning Fabry-Perot etalon (FPI) (Spectra-Physics). The quartz cell with Cd and Kr gas is placed in the oven enabling the temperature stabilization up to 1K. The fluorescence spectrum of cadmium is excited by high frequency Cd lamp. For more detailed see the previous work [23].

The measurements of the pressure effect of the Cd line of 326.1 nm were carried out at temperature 468 K which corresponds to the number density of cadmium N = 4.02 10^{12} cm^{-3}. The Cd density was
calculated using the formula proposed by Dichburn [24]. The perturbed gas Kr pressure ranged from 3 to 95 Torr at room temperature.

2.2. Spectral line profile
If the thermal motion of the emitting atom and its interactions with perturbing atoms are statistically independent, the resultant line shape may be expressed as a Voigt profile which is a convolution of the Gaussian and Lorentzian distributions.

Due to the free thermal motion of the emitting and perturbing atoms, the interaction between the two atoms is treated as statistically independent and the resultant line shape may be expressed by Ballik's formula which is a convolution of Voigt and instrumental Airy profile for ideal FPI [25]:

\[
I(\nu) = \frac{2}{\Omega} \left[ \frac{1}{2} + \sum_{n=1}^{\infty} R^n e^{-n\gamma L} e^{-n^2 D^2/4} \cos \left( \frac{2n\pi \nu}{\Omega} (\nu - \nu_0 - \Delta) \right) \right]
\]

where \( L = \frac{\nu_0'}{\Omega} \) and \( D = \frac{\nu_0''}{\Omega \sqrt{\ln 2}} \), \( \nu_0 \) is the unperturbed frequency of the line, \( \Omega \) is the free spectral range, \( \gamma_L \) and \( \gamma_D \) are half-widths of the Lorentzian and Doppler components of the observed profile, and \( \Delta \) is the pressure shift of the spectral line. Equation (1) is fitted to the measured profile using a least-squares algorithm given by Marquardt [26]. The fitting parameters are the Lorentzian (\( \gamma_L \) cm\(^{-1} \)) and Doppler (\( \gamma_D \) cm\(^{-1} \)) half-widths and the line shift (\( \Delta \) cm\(^{-1} \)).

2.3. Experimental results
Figure 1 shows an example of the experimental and the best fit profile of the 326.1 nm Cd line perturbed by Kr.

Figure 2 show the relation between the Doppler half-width (\( \gamma_D \)) and the perturbing gas pressure (P) from 3 to 95 Torr. Figure 3 shows the plot of the Lorentzian half-width (\( \gamma_L \)) and the shift (\( \Delta \)) of the Cd spectral line 326.1 nm perturbed by Kr as a function of the perturbing gas density (N) at temperature 468 K. The average experimental Doppler half-width (\( \gamma_D \)) amounts to (49.01 ± 1.2) x 10\(^{-3} \) cm\(^{-1} \).

Figure 2. Doppler half-width (\( \gamma_D \)) of the Cd spectral line 326.1 nm plotted against the perturbing gas pressure (in Torr) at temperature 468 K.

It is clear that the Lorentzian half-width (\( \gamma_L \)) and the shift (\( \Delta \)) of the Cd spectral line are linearly dependent on the perturbing gas density N [9, 23]. These dependencies are described by the relations:

\[
\gamma_L = \gamma_L^0 + \beta N \quad \text{and} \quad \Delta = \Delta^0 + \delta N
\]
where \( \gamma_L^o \) and \( \Delta^o \) are the residual half-width and shift of the spectral line. In this experiment, found that \( \gamma_L^o = (2.28 \pm 0.4) \times 10^{-3} \text{ cm}^{-1} \) and the residual value \( \Delta^o = (1.38 \pm 0.3) \times 10^{-3} \text{ cm}^{-1} \). From the slope of the two lines, the pressure broadening (\( \beta \)) and shift (\( \delta \)) coefficients.

Figure 3. Lorentzian half-width (\( \gamma_L \)) and the pressure shift (\( \Delta \)) of the Cd spectral line 326.1 nm perturbed by Kr at temperature 468 K plotted against the perturbing gas density.

3. Theoretical calculation

3.1. Calculation of van der Waals and Lennard–Jones potentials

The experimental results were interpreted using the Lindholm-Foley version of the impact theory using van der Waals (VdW) and Lennard–Jones (LJ) potentials. For more details see [26, 27].

The van der Waals potential is given by:

\[
V(R) = -C_6 / R^6
\]

where \( C_6 \) is the VdW force constant in the given state and \( R \) is the interatomic separation between the radiating and perturbing atoms. To calculate the VdW force constant \( C_6 \) the approximate formula given by Unsöld [28], has been used:

\[
C_6 = e^2 \alpha \langle r^2 \rangle
\]

where \( e \) is the electron charge, \( \alpha \) is the dipole polarizability of the perturbing and \( \langle r^2 \rangle \) is the quantum mechanical mean value of \( r^2 \) in a given state of the radiating atom. The values of \( \langle r^2 \rangle \) have been calculated for both the ground and exited states using the Coulomb approximation:

\[
\langle r^2 \rangle = \left( \frac{1}{2} \right) a_o^2 n_{\text{eff}}^2 \left[ 5n_{\text{eff}}^2 + 1 - 3\ell (\ell + 1) \right]
\]

where \( a_o \) is the Bohr radius, \( \ell \) and \( n_{\text{eff}} \) are the azimuthal and effective quantum numbers. \( \ell = 0, 1 \) for the ground \( ^1S_0 \) and excited \( ^3P_1 \) states respectively.

The LJ potential is given by:

\[
V(R) = C_{12} / R^{12} - C_6 / R^6
\]

where \( C_6 \) and \( C_{12} \) are the attractive and repulsive potential parameters and \( R \) is the interatomic separation between the radiating and perturbing atoms. For calculating the \( c_{12} \) constant, the Hindmarsh [29] formula has been used as:

\[
C_{12} = q(R_A + R_B)^{12}
\]

where \( q = (0.9 \pm 0.3) \times 10^{-16} \text{ erg} \) and \( R_A \) or \( R_B \) denotes the so-called Hindmarsh radius which is defined as the distance from the nucleus of atom A or B at which the unperturbed radial charge density has the value 0.012 a.u. These distances are calculated using the Froese-Fischer program [30] for the Hartree-Fock wave functions [27].

As the Cd intercombination spectral line at 326.1 nm is due to the transition \( ^53P_1 - ^53S_0 \) and the excited state \( ^3P_1 \) have two molecular states \( ^3o^+ \) and \( ^31 \), it is very interested to see which transition is more effected in the broadening and shift of the spectral line, for that we calculate the VdW (\( \Delta C_6^o, \Delta C_6^1 \)) and LJ (\( \Delta C_{12}^o, \Delta C_{12}^1 \)) potentials parameters difference for different transition see Table 1, (\( \Delta C_6, \Delta C_{12} \)) for the \( ^53P_1 - ^53S_0 \) are calculated using the formulas

\[
\Delta C_6 = (2/3)\Delta C_6^o + (1/3)\Delta C_6^1 \quad \text{and} \quad \Delta C_{12} = (2/3)\Delta C_{12}^o + (1/3)\Delta C_{12}^1
\]

The calculated values of the potential parameters differences between the ground and exited states of Cd perturbed by Kr inert gas for the VdW (\( \Delta C_6 \)) and LJ (\( \Delta C_{12} \)) are presented in Table 2.
Table 1. The used symbols for the VdW and LJ potential parameters differences with the corresponding broadening and shift coefficients for the different transitions

| Transition     | VdW parameters | LJ parameters | Broadening Coefficients $\beta$ | Shift Coefficients $\delta$ |
|----------------|----------------|---------------|---------------------------------|----------------------------|
| A $^3\text{o}^+ - X ^1\text{o}^+$ | $\Delta C_6^o$ | $\Delta C_{12}^o$ | $\beta^0$ | $\delta^0$ |
| B $^3\text{I}^1 - X ^1\text{I}^0$ | $\Delta C_6^I$ | $\Delta C_{12}^I$ | $\beta^1$ | $\delta^1$ |
| 5 $^3\text{P}_1 - 5 ^3\text{S}_0$ | $\Delta C_6$ | $\Delta C_{12}$ | B | $\Delta$ |

Table 2. The van der Waals ($\Delta C_6 \times 10^6$ cm$^{-1}$ Å$^6$) and Lennard-Jones ($\Delta C_{12} \times 10^9$ cm$^{-1}$ Å$^{12}$) potential parameters differences between the ground and excited states of Cd perturbed by Kr inert gas

| References                  | VdW parameters | LJ parameters |
|-----------------------------|----------------|---------------|
| This work (VdW-CA)          | --             | --            |
| Roston [10]                 | 1.0326         | 1.1092        |
| Roston [11]                 | 0.1901         | 0.2943        |
| vdW-Grycuk et al. [12]      | 0.2998         | 0.4683        |
| Czajkowski [14]             | 0.0290         | 0.1433        |
| Koperski [16, 17]           | 0.0232         | 0.6660        |
| Czuchaj [18]                | 0.0171         | 1.3227        |
| Czuchaj 19 [19]             | 0.0032         | --            |

3.2. Calculation of the broadening $\beta$ and shift $\delta$ coefficients

The collision broadening and shift coefficients $\beta$ and $\delta$ (in angular frequency units) for the Cd intercombination line 326.1 using both van der Waals and Lennard-Jones potential parameters have been calculated as follows:

For the Van der Waal’s potential, the broadening $\beta$ and shift $\delta$ coefficients are calculated using the following formulas [31, 32]:

$$\beta = 8.16\sqrt{\frac{3}{5}} (\Delta C_6)^{2/5}$$

where $\sqrt{\frac{3}{5}}$ is the mean relative velocity. In the case of the Lennard-Jones potential, $\Delta C_6$ and $\Delta C_{12}$ are the potential parameters difference between the ground and excited states, then $\beta$ and $\delta$ are calculated using Hindmarsh et al. [29]:

$$\beta = 8\pi (3\pi/8)^{2/5} \sqrt{\frac{3}{5}} (\Delta C_6)^{2/5} B(\alpha)$$

$$\delta = 2\pi (3\pi/8)^{2/5} \sqrt{\frac{3}{5}} (\Delta C_6)^{2/5} S(\alpha)$$

where the broadening $B(\alpha)$ and shift $S(\alpha)$ functions are given by:

$$B(\alpha) = \int_0^\infty x \sin^2 0.5(\alpha x^{1/5} - x^{-5}) \, dx$$

$$S(\alpha) = \int_0^\infty x \sin(\alpha x^{1/5} - x^{-5}) \, dx$$

and

$$\alpha = 0.536 \sqrt{\frac{6}{5}} (\Delta C_6)^{1/15} \Delta C_{12}$$

The two functions $B(\alpha)$ and $S(\alpha)$ for different values of $\alpha$ are tabulated in Ref. [29]. The experimental, calculated and the published values of $\beta$ and $\delta$ are presented in Table 3. To follow the labeled of the broadening $\beta$ and shift $\delta$ coefficients see Table I.

It is seen from Table III, the obtained experimental results for the broadening and shift coefficients $\beta$ and $\delta$ are agreement with both the experimental result obtained by Brym and Domysfawska [9] and with theoretical values calculated using the Coulomb approximation and VdW potential. Concerning the
comparison between the obtained results and those calculated using different published data can be concluded as:

1- The VdW potential gives an agreement results for the broadening and shift coefficients ($\beta$ and $\delta$) with the experimental results, specially using the potential parameters obtained by [10-12, 16-17], but it gives a poor agreement with the potential obtained from [14,18-19]. For that the long range interaction is more effected in the broadening and shift of the spectral lines.

2- The LJ potential gives a good agreement results, using the potential parameters obtained by [10] and for the shift parameter using [16-17], but it gives a poor agreement with the Coulomb approximation and with that results calculated using the potential obtained by [14,18-19].

3- From the analysis of the obtained results, it was found that the more shallow state 31 is more effected than the deepest state 30 in this interaction.

| Table 3. The experimental and calculated values of the broadening and shift coefficients $\beta$ and $\delta$ (in units of $10^{-20}$ cm$^{-1}$/atom cm$^{-3}$) of the Cd line 326.1 nm perturbed by Kr inert gas and the corresponding experimental and theoretical published values |
|---------------------------------------------------------------|------------------|-----------------|-----------------|-----------------|-----------------|
| References | Broadening Coefficient | Shift Coefficient |
| --- | --- | --- | --- | --- | --- |
| This work | $0.974 \pm 0.05$ | $-0.267 \pm 0.04$ |
| Brym and Domysfawska [9] | $1.00 \pm 0.03$ | $-0.27 \pm 0.03$ |
| This work (VdW-CA) | $0.906$ | $-0.323$ |
| Roston [10] | $1.1420$ | $1.1462$ | $1.145$ | $-0.31$ | $-0.32$ | $-0.317$ |
| Roston [11] | $0.7222$ | $0.8599$ | $0.818$ | $-0.26$ | $-0.31$ | $-0.291$ |
| vdW-Grycuk et al. [12] | $0.8664$ | $1.0356$ | $0.984$ | $-0.31$ | $-0.37$ | $-0.351$ |
| Czajkowski [14] | $0.3405$ | $0.6449$ | $0.570$ | $-0.12$ | $-0.23$ | $-0.203$ |
| Koperski [16, 17] | $0.3108$ | $1.1922$ | $1.021$ | $-0.11$ | $-0.43$ | $-0.364$ |
| Czuchaj [18] | $0.2754$ | $1.568$ | $1.337$ | $0.098$ | $-0.56$ | $-0.477$ |
| Czuchaj [19] | $0.1412$ | $-0.05$ | $-0.05$ | $-0.05$ | $-0.05$ | $-0.05$ |
| This work (LJ-CA) | $-0.601$ | $-0.315$ |
| Roston [10] | $1.148$ | $1.139$ | $1.131$ | $-0.27$ | $-0.34$ | $-0.252$ |
| Czajkowski [14] | $0.5167$ | $0.523$ | $0.399$ | $0.04$ | $-0.07$ | $-0.089$ |
| Koperski [16, 17] | $0.482$ | $1.160$ | $0.997$ | $0.044$ | $-0.53$ | $-0.499$ |
| Czuchaj [18] | $0.438$ | $1.429$ | $1.364$ | $0.078$ | $-0.58$ | $-0.441$ |
| Czuchaj [19] | $0.3247$ | $0.038$ | $0.038$ | $0.038$ | $0.038$ | $0.038$ |

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