

# ANALYSIS OF BROADENING AND SHIFT OF THE 326.1 nm Cd LINE BY He AND Ne

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(Received June 13, 1996)

The experimental values of pressure broadening and shift parameters of the 326.1 nm Cd line perturbed by He and Ne, are compared with those calculated from the adiabatic and nonadiabatic approaches to the impact theory for different interaction potentials.

PACS numbers: 32.70.Jz, 33.70.Jg, 34.20.Cf

## 1. Introduction

In an earlier paper from this laboratory [1] results of measurements of the pressure broadening and shift of the  $^{114}\text{Cd}$  326.1 nm ( $5^1S_0-5^3P_1$ ) intercombination line perturbed by He and Ne were reported. The measurements were performed for pressures of the perturbing atoms below 100 Tr, and the experimental values of the pressure broadening ( $\beta$ ) and shift ( $\delta$ ) coefficients were compared with those resulting from the Lindholm-Foley impact theory assuming the interaction potential to be given in the Lennard-Jones form. It should be emphasized that for the Cd-rare gas (Cd-Rg) systems the application of the Lindholm-Foley treatment is not completely justified because the Cd-Rg system in the ground state ( $\text{Cd}(5^1S_0)+\text{Rg}(^1S_0)$ ) is described by one potential curve  $X^{10^+}$  only whereas in the excited state ( $\text{Cd}(5^3P_1)+\text{Rg}(^1S_0)$ ) there are two potential curves  $A^{30^+}$  and  $B^31$ . The observed 326.1 nm Cd line is thus a superposition of the  $A^{30^+}-X^{10^+}$  and  $B^31-X^{10^+}$  transitions. This is why the calculations of the  $\beta$  and  $\delta$  coefficients should be made using the molecular potentials  $V_X$ ,  $V_A$ ,  $V_B$  describing the following quasi-molecular states:  $X^{10^+}$ ,  $A^{30^+}$  and  $B^31$ , respectively.

Such calculations, performed in the framework of the Baranger [2] impact theory, using the scattering  $S$ -matrix formalism in semi-classical approach were already done for Na perturbed by H, He, Ar,  $\text{N}_2$ ,  $\text{H}_2$  [3-8], Cs perturbed by Xe [9] and recently for the self-broadening in helium [10, 11].

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The purpose of this paper is to calculate the values of the pressure broadening and shift coefficients for  $^{114}\text{Cd}$  326.1 nm ( $5^1S_0-5^3P_1$ ) intercombination line perturbed by He and Ne, in the framework of the Baranger [2] impact theory, using  $S$ -matrix formalism. The calculations presented in this paper were performed using the molecular potentials described in Sec. 3.

## 2. Pressure broadening and shift coefficients for Cd-He and Cd-Ne systems

Following Baranger [2] the intensity distribution  $I(\omega)$  in a broadened line can be written in the Lorentzian form

$$I(\omega) = \frac{\gamma}{2\pi} \frac{1}{(\omega - \omega_0 - \Delta)^2 + (\gamma/2)^2}, \quad (1)$$

where  $\gamma$  is the half-width (FWHM) and  $\Delta$  is the pressure shift of the line. Both  $\gamma$  and  $\Delta$  are proportional to the number density  $N$  of the perturbing atoms, i.e.  $\gamma = \beta N$  and  $\Delta = \delta N$ , where  $\beta$  and  $\delta$  are the pressure broadening and shift coefficients, respectively.

In the Baranger [2] formulation these coefficients are given by

$$\frac{\beta}{2} + i\delta = 2\pi \left\langle v \int_0^{+\infty} d\rho \rho \{1 - S_{ii}S_{ff}^{-1}\}_{\text{Ang.Av.}} \right\rangle. \quad (2)$$

Here  $v$  denotes the relative velocity of the colliding atoms and  $\rho$  is the impact parameter. The symbol  $\langle \dots \rangle$  denotes the averaging over Maxwellian distribution of velocities, and  $\{ \dots \}_{\text{Ang.Av.}}$  denotes the angular averaging.  $S_{ii}$  and  $S_{ff}$  denote the elements of the scattering  $S$ -matrix for the initial (i) and final (f) state of the radiating atom, respectively.

The angular average  $\{S_{ii}S_{ff}^{-1}\}_{\text{Ang.Av.}}$  is given by the following equation [12, 13]:

$$\begin{aligned} \{S_{ii}S_{ff}^{-1}\}_{\text{Ang.Av.}} = & \sum_{m_i, m_f, m'_i, m'_f, M} (-1)^{2j_i + m_i + m'_i} \begin{pmatrix} j_f & 1 & j_i \\ m_f & M & -m_i \end{pmatrix} \\ & \times \begin{pmatrix} j_f & 1 & j_i \\ m'_f & M & -m'_i \end{pmatrix} \langle j_i m_i | \hat{S} | j_i m'_i \rangle \langle j_f m'_f | \hat{S}^{-1} | j_f m_f \rangle. \end{aligned} \quad (3)$$

We treat the collision between emitter and perturber semi-classically, using the straight line trajectory approximation. We assume that the emitter is fixed in the beginning of the collisional reference frame while the perturber moves on the straight line trajectory with the constant velocity  $v$  and impact parameter  $\rho$ . The distance  $R$  between emitter and perturber is thus given by  $R = \sqrt{\rho^2 + v^2 t^2}$ .

In order to describe the collision process, we follow Baranger [2] and use two different reference frames:

- 1) fixed collisional frame  $OX_1Y_1Z_1$  with the quantization axis  $OZ_1$  perpendicular to the collision plane and  $OY_1$  axis directed along the impact parameter  $\rho$ ,
- 2) molecular frame  $OXYZ$ , rotating around  $OZ_1$  axis, with the quantization axis  $OZ$  directed along the  $\mathbf{R}$  vector and  $OY$  axis directed along  $OZ_1$  axis of the collisional frame (see Fig. 1). Such a choice of the  $OZ$  axis is due to the axial symmetry of the interaction potential  $V(R)$ .

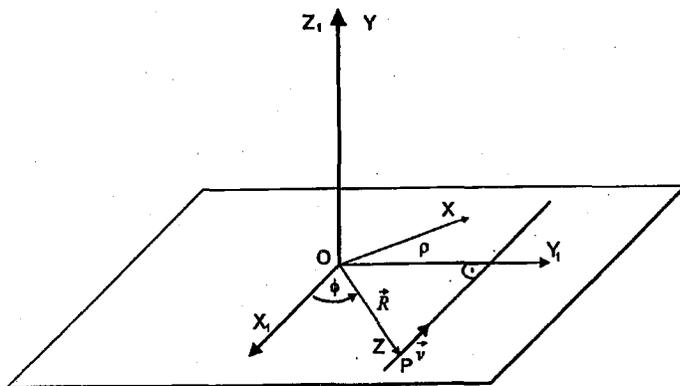


Fig. 1. Two reference frames used for describing the collision between perturber  $P$  moving with velocity  $v$  and impact parameter  $\rho$  and emitter  $O$ :  $OX_1Y_1Z_1$  is the fixed collisional frame and  $OXYZ$  is the molecular frame rotating around  $OZ_1$  axis.

The Hamiltonian of the Cd-Rg system may be written as

$$H = H_0 + V(R), \quad (4)$$

where  $H_0 = H_E + W$  is the Hamiltonian of the emitter-perturber system for  $R \rightarrow \infty$  and  $H_E$  is the sum of Hamiltonians of the unperturbed Cd and Rg atoms including electrostatic interaction in the Cd and Rg atoms,  $W$  is the spin-orbit interaction in the Cd atom.

As the collision is the time dependent process one should solve the time dependent Schrödinger equation

$$i\hbar \frac{\partial |\Psi(t)\rangle}{\partial t} = H |\Psi(t)\rangle. \quad (5)$$

The state vector  $|\Psi(t)\rangle$  may be expressed as a series

$$|\Psi(t)\rangle = \sum_k a_k(t) \exp\left(-\frac{i}{\hbar} E_k t\right) |k\rangle, \quad (6)$$

where  $|k\rangle = |n_k l_k s_k j_k m_k\rangle_E |n 0 0\rangle_P$  (where  $|n 0 0\rangle_P$  is an eigenvector of the perturber in the state  $n^1S_0$ ). The expansion coefficients  $a_k(t)$  satisfy the well-known relation

$$i\hbar \dot{a}_k(t) = \sum_s a_s(t) \langle k | V | s \rangle \exp\left[\frac{i}{\hbar} (E_k - E_s) t\right]. \quad (7)$$

The  $S$ -matrix elements  $S_{sk}$  can be obtained as the asymptotic solutions of Eqs. (7) for  $t \rightarrow \infty$  with the initial conditions  $a_k(t = -\infty) = \delta_{ik}$ .

In the Cd-Rg (Rg = He, Ne) systems the difference of the interaction energy  $\Delta V_{A'A}$  for all potentials discussed in Sec. 3, satisfy the relation  $\Delta V_{A'A} < \Delta W = \langle 5^3P_1 | W | 5^3P_1 \rangle - \langle 5^3P_0 | W | 5^3P_0 \rangle$  even for small interatomic distances. For example for the Cd-Ne system and the Morse potential we get  $\Delta V_{A'A} \approx \Delta W$  for  $R \approx 5$  a.u. For such small  $R$  values  $\{1 - S_{ii} S_{ii}^{-1}\}_{\text{Ang. Av.}}$ , occurring in formula (2) oscillates so rapidly (see Fig. 2 and [3, 5, 8]) that in calculations of this integral it may be replaced by its mean value [38]. Therefore we may assume that for the

Cd-Rg (Rg = He, Ne) systems we have the Hund case "c". In this case the interaction matrix  $V$  is diagonal in the  $|\Omega\rangle$  representation, where  $\Omega$  is the absolute value of the projection of the total momentum  $j$  on the internuclear axis of the Cd-Rg molecule.

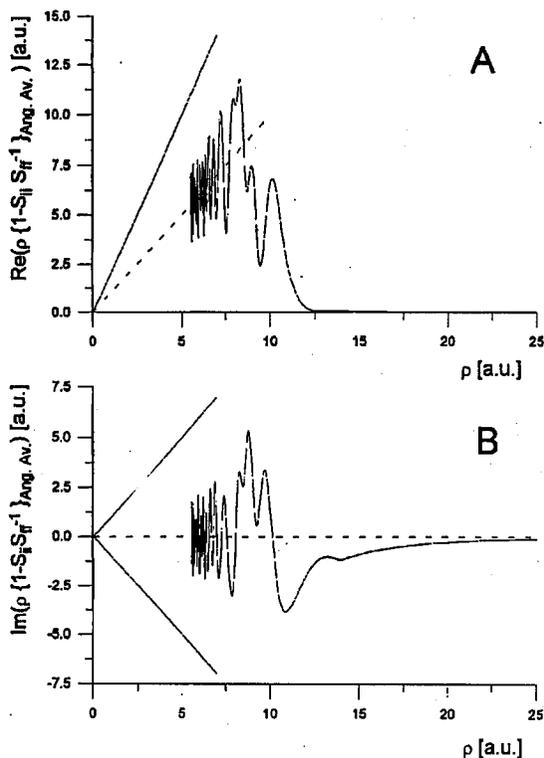


Fig. 2. Dependence of integrands in Eq. (2) on the impact parameter  $\rho$  for CSP potential: (A) real part responsible for line broadening, (B) imaginary part responsible for line shift. The straight lines represent the oscillation limits of integrands in Eq. (27) and (28) (adiabatic approximation).

The experimental investigations of the Cd-He and Cd-Ne collisions [14, 15] show that the quenching cross-section of the  $5^3P_1$  state as well as the transitions between the levels of the fine structure are small. Therefore in calculations of the  $S$ -matrix elements these nonadiabatic effects were omitted. However, we have included the nonadiabatic effects due to the rotation of the molecular axis. In such a case set of Eqs. (7) leads to four equations. One is for the  $5^1S_0$  state, with the  $a'_0(t)$  coefficient, and three for the  $5^3P_1$  state with the  $a_{-1}(t)$ ,  $a_0(t)$  and  $a_{+1}(t)$  for  $m_k = -1, 0, +1$ , respectively. The element of the interaction matrix is given by

$$\begin{aligned} \langle k|V|s\rangle &= {}_P \langle n_0 0 0 | {}_E \langle n_k l_k s_k j_k m_k | V | n_s l_s s_s j_s m_s \rangle {}_E | n 0 0 \rangle {}_P \\ &= \langle j_k m_k | V | j_s m_s \rangle = \langle j m_k | V | j m_s \rangle. \end{aligned} \quad (8)$$

The relation between the elements of the interaction matrix  $V$  given in collisional  $|jm\rangle$  and rotating molecular  $|\Omega\rangle$  reference frames is given by elements of the reduced rotation matrix  $d_{\Omega,m}^j$  (see e.g. [16])

$$\langle jm_k | V | jm_s \rangle = \sum_{\Omega} (-1)^{\Omega - m_k} e^{-i\phi(m_k - m_s)} d_{-\Omega, -m_k}^j \left( \frac{\pi}{2} \right) d_{\Omega, m_s}^j \left( \frac{\pi}{2} \right) \langle \Omega | V | \Omega \rangle, \quad (9)$$

where

$$\langle \Omega | V | \Omega \rangle = \begin{cases} V_X & \text{for the } 5^1S_0 \text{ state } (\Omega = 0), \\ V_A & \text{for the } 5^3P_1 \text{ state } (\Omega = 0), \\ V_B & \text{for the } 5^3P_1 \text{ state } (\Omega = 1). \end{cases} \quad (10)$$

The interaction matrix (see e.g. [4, 10]) is Hermitian and fulfils the following conditions:

$$\langle l_k s_k j_k m_k | V | l_s s_s j_s m_s \rangle = (-1)^{j_s + j_k} \langle l_k s_k j_k - m_k | V | l_s s_s j_s - m_s \rangle^*, \quad (11)$$

$$\langle l_k s_k j_k m_k | V | l_s s_s j_s m_s \rangle \neq 0 \quad \text{for } m_k - m_s = 0, \pm 2, \pm 4, \dots \quad (12)$$

Following (9) the non-zero elements of the interaction matrix given in the collisional frame are:

for the  $5^1S_0$  state

$$\langle 00 | V | 00 \rangle = V_X, \quad (13)$$

for the  $5^3P_1$  state

$$\langle 10 | V | 10 \rangle = V_B, \quad (14)$$

$$\langle 11 | V | 11 \rangle = \langle 1 - 1 | V | 1 - 1 \rangle = \frac{1}{2}(V_A + V_B) = V_1, \quad (15)$$

$$\langle 11 | V | 1 - 1 \rangle = \langle 1 - 1 | V | 11 \rangle^* = \frac{1}{2}(V_B - V_A)e^{-2i\phi} = f e^{-2i\phi}. \quad (16)$$

Finally the set of Eqs. (7) is given in the following form:

for the  $5^1S_0$  state we have one equation

$$i\hbar \dot{a}'_0(t) = a'_0(t) V_X, \quad (17)$$

for the  $5^3P_1$  state

$$i\hbar \dot{a}_0(t) = a_0(t) V_B, \quad (18)$$

$$i\hbar \dot{a}_{-1}(t) = a_{-1}(t) V_1 + a_{+1}(t) f e^{+2i\phi}, \quad (19)$$

$$i\hbar \dot{a}_{+1}(t) = a_{-1}(t) f e^{-2i\phi} + a_{+1}(t) V_1, \quad (20)$$

we have one (18) separated and two (19), (20) coupled equations.

### 2.1. Adiabatic approximation

In the adiabatic approximation we assume that we have one quantization axis directed along the internuclear axis of the Cd-Rg molecule. It corresponds to the assumption that only non-zero elements are  $\langle jm_s | V | jm_s \rangle = \langle \Omega | V | \Omega \rangle$ . In such a case Eqs. (7) may be written in the form

$$i\hbar \dot{a}'_0(t) = a'_0(t) V_X, \quad (21)$$

$$i\hbar\dot{a}_0(t) = a_0(t)V_A, \quad (22)$$

$$i\hbar\dot{a}_{-1}(t) = a_{-1}(t)V_B, \quad (23)$$

$$i\hbar\dot{a}_{+1}(t) = a_{+1}(t)V_B. \quad (24)$$

Thus we have three separated equations for the  $^3P_1$  state. Solving them we get the  $S$ -matrix elements, and from Eqs. (2) and (3) we get

$$\beta = \frac{1}{3}\beta_{A-X} + \frac{2}{3}\beta_{B-X}, \quad (25)$$

$$\delta = \frac{1}{3}\delta_{A-X} + \frac{2}{3}\delta_{B-X}. \quad (26)$$

Here  $\beta_{A-X}$  and  $\delta_{A-X}$  (or  $\beta_{B-X}$  and  $\delta_{B-X}$ ) denote the pressure broadening and shift coefficients corresponding to the  $A^30^+-X^10^+$  (or  $B^31-X^10^+$ ) transition in the Cd-Rg quasi-molecule which can be written in the form

$$\beta_{i-X} = 4\pi \left\langle v \int_0^{+\infty} d\rho \rho [1 - \cos(\eta_{i-X}(v, \rho))] \right\rangle, \quad (27)$$

$$\delta_{i-X} = 2\pi \left\langle v \int_0^{+\infty} d\rho \rho \sin(\eta_{i-X}(v, \rho)) \right\rangle, \quad (28)$$

where the index  $i$  corresponds either to the  $A^30^+$  or  $B^31$  state. It is seen that Eqs. (27) and (28) are identical to the Lindholm-Foley formulae for the  $A^30^+-X^10^+$  and  $B^31-X^10^+$  transition. The phase shift  $\eta_{i-X}$  is given by

$$\eta_{i-X} = \frac{1}{\hbar} \int_{-\infty}^{+\infty} [V_i(t) - V_X(t)] dt. \quad (29)$$

All the calculations performed in this paper were carried out using classical straight-line trajectories.

### 3. Interaction potentials for the Cd-He and Cd-Ne systems

For the Cd-He and Cd-Ne systems there are theoretical potential curves calculated from the pseudopotentials method [17] and using the effective Hamiltonian method [18]. The spectroscopic constants appearing in the Morse potential were determined only for the Cd-Ne system [19-24]; unfortunately there are no such experimental data for the Cd-He system.

#### 3.1. Pseudopotential method

Czuchaj et al. [17] calculated the adiabatic potentials of the Cd-Rg systems (Rg = He, Ne) performing the self-consistent field/configuration interaction (SCF/CI) calculations. The Cd-Rg system was approximated as a two-valence-electron system. In the pseudopotential calculations an effective potential was defined as a potential experienced by the valence electron both from the  $Cd^{2+}$  core and the Rg atom. Such a pseudopotential represents the effect of incomplete screening of the nuclear charge due to the core electrons, it also simulates the antisymmetry effect due to the Pauli principle by a repulsive potential, and it can also include the polarization interaction. Since the molecular pseudopotential calculations with the  $l$ -independent Gombas-type statistical pseudopotentials, as

proposed by Baylis [25], certainly fail for the lightest rare gases (He, Ne), Czuchaj et al. [17] used the semi-empirical  $l$ -dependent pseudopotentials to describe the interaction of the Cd valence electrons with Cd<sup>2+</sup> core and Rg atom.

It should be noted that the values of the  $V_X$ ,  $V_A$  and  $V_B$  potentials given in paper [17] were recently amended by Czuchaj [26].

These potentials were calculated in the range of the internuclear distances  $5.5 \leq R \leq 14.0$  a.u. For low densities of the perturbing gases, i.e. for the conditions where the impact theory is applicable, the main contribution to the line shifts is due to the distant flights of the perturbers (c.f. e.g. [27]), therefore it is necessary to know the values of the interaction potentials for the large values of the interatomic distances. This is why we had to extend these potentials. The extension was made in the following way. In the most distant point (with  $R = R_d$ ) of each potential curve  $V(R)$  we stitched the van der Waals type curve  $U(R) = KR^{-6}$ . The  $K$  constants were determined from the continuity condition of the curve calculated by Czuchaj [26] and stitched potentials i.e.  $V(R_d) = U(R_d) = KR_d^{-6}$ . Such extended potentials hereafter will be denoted as CSP. Results of calculations for the Cd-He system are presented in Table I, and for Cd-Ne system in Table II.

TABLE I

The experimental and theoretical values of the pressure broadening  $\beta$  and shift  $\delta$  coefficients (in units  $10^{-20} \text{ cm}^{-1}/\text{atom} \cdot \text{cm}^{-3}$ ) for the <sup>114</sup>Cd 326.1 nm line perturbed by helium. Numbers in parenthesis represent the standard deviation of the least squares fit. Notations explained in the text.

	$\beta$		$\delta$	
	adiabatic	nonadiabatic	adiabatic	nonadiabatic
CSP	1.40	1.27	0.15	0.08
ZL/CSP	0.92	0.96	0.22	0.12
Exp [1]	1.22(0.03)		0.02(0.02)	

TABLE II

The experimental and theoretical values of the pressure broadening  $\beta$  and shift  $\delta$  coefficients (in units  $10^{-20} \text{ cm}^{-1}/\text{atom} \cdot \text{cm}^{-3}$ ) for the <sup>114</sup>Cd 326.1 nm line perturbed by neon. Numbers in parenthesis represent the standard deviation of the least squares fit. Notations explained in the text.

	$\beta$		$\delta$	
	adiabatic	nonadiabatic	adiabatic	nonadiabatic
CSP	0.84	0.74	0.08	0.06
ZL/CSP	0.72	0.68	0.08	0.17
ZL/Morse	0.76	0.58	-0.26	-0.15
Morse	2.27	1.41	-0.75	-0.60
Exp [1]	0.70(0.02)		-0.13(0.01)	

### 3.2. Effective Hamiltonian method

In paper [18] the interaction potentials for the  $\text{Cd}(5^3P_J) + \text{Rg}$  ( $\text{Rg} = \text{He}, \text{Ne}$ ) systems were calculated using the effective Hamiltonian method [28] on the basis of approach given by [32, 33]. This formulation takes into account an intermediate type of coupling of the electron angular momenta of the excited atom. The matrix elements of the effective Hamiltonian in the basis of quasi-molecular diabatic wave functions  $|^1,^3P_J\Omega\rangle_{\text{ic}} = |\text{Cd}(5^1,^3P_J)\Omega\rangle_{\text{ic}}^{\text{at}}|\text{Rg}(^1S_0)\rangle$  (where  $|\text{Cd}(5^1,^3P_J)\Omega\rangle_{\text{ic}}^{\text{at}}$  — the atomic wave function of the intermediate type of coupling and  $\Omega$  is the projection of  $J$  on internuclear axis) are expressed by the potentials  $^1,^3H_\sigma(R)$  with zero projection  $m = 0$  of the excited electron orbital momentum  $l$  on the internuclear axis and by potentials  $^1,^3H_\pi(R)$  with  $|m| = 1$ . The potentials  $^1,^3H_{\sigma,\pi}(R)$  describe the  $\text{Cd}(5s5p)$  interaction in the  $^1,^3\Sigma^+$  and  $^1,^3\Pi$  states, respectively, calculated without the inclusion of the spin-orbit interaction.

In order to calculate the  $^1,^3H_\sigma(R)$  and  $^1,^3H_\pi(R)$  potentials [18] the one-electron method of pseudopotential [29–31, 34, 35] was used.

During the course of this investigation the interaction potentials for the  $\text{Cd}(5^3P_J) + \text{Rg}$  ( $\text{Rg} = \text{He}, \text{Ne}$ ) systems were recalculated up to  $R = 25$  a.u. The values of these potentials are listed in Appendix. As was already noted, the distant flights play very important role in the calculations of the  $\delta$  coefficients. This is why we had to extend these potentials using the stitching procedure identical to that described in previous section.

Since the above method cannot be applied to the ground state ( $5s^2$ ) of the Cd atom, the  $\beta$  and  $\delta$  parameters were calculated using for the ground state the CSP potential curves. The calculated values of the  $\beta$  and  $\delta$  parameters for the Cd–He and Cd–Ne systems are listed in Tables I and II, respectively, where they are marked ZL/CSP.

For the Cd–Ne system the calculations of the  $\beta$  and  $\delta$  parameters were also performed using for the ground state the potential curve given by the Morse function (for details see next subsection). The results of these calculations are listed in Table II, and marked ZL/Morse.

### 3.3. Morse potential

The spectroscopic investigations of the Cd–Ne system yielded the quantitative data on the vibrational bands structure [19–23] as well as the rotation-vibration bands structure [20]. The spectroscopic constants for the following molecular states of the Cd–Ne molecule:  $X^10^+$  [19–24],  $A^30^+$  [19, 20, 22–24] and  $B^31$  [19, 22] have been derived.

The most complete set of experimental results for the  $A$ – $X$  band is given by Czajkowski et al. [24] who corrected the previous analysis for the  $X^10^+$  and  $A^30^+$  states given in [22]. In the present study we assumed a Morse potential given by

$$V(R) = D_e \left[ e^{-2\kappa(R-R_e)} - 2e^{-\kappa(R-R_e)} \right], \quad (30)$$

where

$$\kappa = \sqrt{\frac{8\pi^2 c \mu \omega_e x_e}{h}}, \quad (31)$$

and  $D_e$  is the well depth,  $R_e$  is the position of equilibrium and  $\omega_e x_e$  is the anharmonicity constant.

For the  $X^10^+$  and  $A^30^+$  states, we used the spectroscopic constants ( $D_e$ ,  $R_e$ ,  $\omega_e x_e$ ) given in [24].

The latest results on the  $B-X$  band are given in paper [22] and are generally consistent with earlier results reported in paper [19]. The values of  $D_e$ ,  $R_e$ ,  $\omega_e x_e$  constants for the  $B^31$  state were taken from paper [22].

The calculated values of the  $\beta$  and  $\delta$  parameters for the Cd-Ne system with the assumption of the Morse potential are listed in Table II, and marked Morse.

#### 4. Results and discussion

The calculations of the pressure broadening  $\beta$  and shift  $\delta$  coefficients were performed with the assumption that the averaging over the Maxwellian distribution of velocities may be replaced by putting in all equations the mean value of the relative emitter-perturber velocity. This approximation was used by many authors and usually it gives no significant errors.

The differential equations (17), (18), (19) and (20) were solved numerically using the fourth-order Runge-Kutta algorithm. The calculations of the  $S$ -matrix elements for a given potential were performed for the  $\rho$  values depending on the range of a potential. The lower limit  $\rho_{\min}$  was about 5.00–6.25 a.u. (depending on the kind of potential), the upper limit  $\rho_{\max}$  was 60.00 a.u. We have checked that the values of  $\rho$  greater than  $\rho_{\max} = 60$  a.u. had no influence on the value of the integral (2). The calculations of the  $\rho$ -integrals were performed numerically with the integration step equal to 0.01 a.u. taking maximal care of the oscillations of the integrands. In the range of small  $\rho$  values (less than  $\rho_{\min}$ ), where the  $S$ -matrix values are not defined, we used the Anderson approximation [38] (dashed line in Fig. 2).

Tables I and II show the values of the pressure broadening  $\beta$  and shift  $\delta$  coefficients for the  $^{114}\text{Cd}$  326.1 nm line perturbed by helium and neon, respectively. The calculations were made in the adiabatic approximation and with the inclusion of the rotation of the internuclear axis (using Eqs. (18)–(20) instead of (22)–(24) ones).

In Table I the results of calculation for CSP and ZL/CSP potentials are presented. As can be seen from the table the best agreement between the calculated and experimental value of  $\beta$  and  $\delta$  coefficients is obtained in case of nonadiabatic calculations for CSP potential, especially for  $\beta$  coefficient. For the ZL/CSP potential the agreement both for  $\beta$  and  $\delta$  coefficients is much worse. Though the nonadiabatic calculations have given better agreement between theoretical and experimental results, the obtained improvement is not satisfactory, especially for the shift  $\delta$  coefficients.

Results of calculations presented in Table II were made for CSP, ZL/CSP, ZL/Morse and Morse potentials. As can be seen for the CSP and ZL/CSP potentials good agreement with experimental results for  $\beta$  coefficients and disagreement for  $\delta$  coefficients is obtained, irrespective of method of calculations. Especially good agreement is for  $\delta$  coefficients computed from nonadiabatic calculations using ZL/Morse potential. The worst agreement between calculated and experimental

$\beta$  and  $\delta$  values is obtained for the Morse potential. It should be noted that adiabatic calculations of  $\beta$  and  $\delta$  coefficients for Morse potential for Cd-Ar [36] and Cd-Kr [37] systems gave satisfactory agreement between calculated and experimental values of  $\beta$  coefficient and worse for  $\delta$  coefficient. It should be thought that  $D_e$ ,  $\omega_e x_e$  and  $R_e$  spectroscopic constants for the  $X^{10+}$  state were determined correctly because  $\beta$  and  $\delta$  coefficient calculated for ZL/Morse potential in which the ground state potential is the Morse one (see Sec. 3) are in reasonable agreement with experimental values. The above consideration and adiabatic calculations of  $\beta_{i-X}$  (27) and  $\delta_{i-X}$  (28) parameters enable us to suppose that one of spectroscopic constants for  $B^31$  state is probably incorrect.

## 5. Conclusions

As it can be seen from Tables I and II the inclusion of the rotation of the interatomic axis leads to a better agreement of calculated values of  $\beta$  and  $\delta$  with experiment although the improvement of the agreement is not fully satisfactory. The reason that some disagreements between theoretical and experimental values of  $\beta$  and  $\delta$  still exist seems to be the quality of the interatomic potentials for Cd-Rg. As we have already noted in Sec. 3 the Czuchaj potentials are tabulated up to  $R = 14.5$  a.u. In order to improve the agreement of the calculated  $\beta$  and  $\delta$  values with experiment we had to extrapolate the potentials by stitching them with the van der Waals potential for large  $R$ .

Figure 2 shows the plots of the integrand in Eq. (2) on the impact parameter  $\rho$  for the CSP potential. As it is seen for  $\rho$  between 12 and 25 a.u. the imaginary part of the integrand which is responsible for the magnitude of the pressure shift of the line is essentially different from zero, whereas the real part responsible for the width is practically equal to zero. We can thus conclude that the accurate knowledge of the potentials for large  $\rho$  is important in order to obtain the reliable values of the line profile parameters, first of all of the shift coefficient. For light perturbers (He, Ne) the potentials should be known with high accuracy up to the interatomic distances 50 a.u.

In conclusion we should emphasize that the knowledge of very precise experimental values of the width and shift parameters may provide critical test of accuracy of the theoretical *ab initio* potentials at large interatomic separations.

## Acknowledgment

The authors wish to express their gratitude to Professor J. Szudy for fruitful discussions and valuable help in the preparation of the manuscript.

When this work was made one of the authors (R.C.) was the scholarship-holder of the Foundation for Polish Science.

This work was partially supported by a grant No. 673/P03/96/10 (2 P03B 005 10) from the Committee for Scientific Research.

## Appendix

The values of the ZL potentials calculated in this work.

R [a.u.]	V(R) [a.u.]			
	Cd-He		Cd-Ne	
	$\Omega = 0^+$	$\Omega = 1$	$\Omega = 0^+$	$\Omega = 1$
6.00	$-3.476 \times 10^{-4}$	$1.063 \times 10^{-3}$	$-7.095 \times 10^{-4}$	$-1.175 \times 10^{-4}$
6.25	$-2.752 \times 10^{-4}$	$9.365 \times 10^{-4}$	$-5.643 \times 10^{-4}$	$-1.954 \times 10^{-4}$
6.50	$-2.194 \times 10^{-4}$	$7.926 \times 10^{-4}$	$-4.516 \times 10^{-4}$	$-2.526 \times 10^{-4}$
6.75	$-1.761 \times 10^{-4}$	$6.474 \times 10^{-4}$	$-3.636 \times 10^{-4}$	$-2.863 \times 10^{-4}$
7.00	$-1.422 \times 10^{-4}$	$5.128 \times 10^{-4}$	$-2.945 \times 10^{-4}$	$-2.992 \times 10^{-4}$
7.25	$-1.156 \times 10^{-4}$	$3.951 \times 10^{-4}$	$-2.399 \times 10^{-4}$	$-2.964 \times 10^{-4}$
7.50	$-9.455 \times 10^{-5}$	$2.970 \times 10^{-4}$	$-1.965 \times 10^{-4}$	$-2.830 \times 10^{-4}$
7.75	$-7.716 \times 10^{-5}$	$2.178 \times 10^{-4}$	$-1.617 \times 10^{-4}$	$-2.630 \times 10^{-4}$
8.00	$-6.346 \times 10^{-5}$	$1.557 \times 10^{-4}$	$-1.338 \times 10^{-4}$	$-2.396 \times 10^{-4}$
8.25	$-5.260 \times 10^{-5}$	$1.080 \times 10^{-4}$	$-1.113 \times 10^{-4}$	$-2.151 \times 10^{-4}$
8.50	$-4.388 \times 10^{-5}$	$7.214 \times 10^{-5}$	$-9.301 \times 10^{-5}$	$-1.909 \times 10^{-4}$
8.75	$-3.682 \times 10^{-5}$	$4.567 \times 10^{-5}$	$-7.811 \times 10^{-5}$	$-1.680 \times 10^{-4}$
9.00	$-3.108 \times 10^{-5}$	$2.647 \times 10^{-5}$	$-6.590 \times 10^{-5}$	$-1.468 \times 10^{-4}$
9.25	$-2.637 \times 10^{-5}$	$1.282 \times 10^{-5}$	$-5.583 \times 10^{-5}$	$-1.277 \times 10^{-4}$
9.50	$-2.248 \times 10^{-5}$	$3.350 \times 10^{-6}$	$-4.751 \times 10^{-5}$	$-1.107 \times 10^{-4}$
9.75	$-1.926 \times 10^{-5}$	$-3.034 \times 10^{-6}$	$-4.058 \times 10^{-5}$	$-9.568 \times 10^{-5}$
10.00	$-1.657 \times 10^{-5}$	$-7.158 \times 10^{-6}$	$-3.480 \times 10^{-5}$	$-8.256 \times 10^{-5}$
10.50	$-1.241 \times 10^{-5}$	$-1.100 \times 10^{-5}$	$-2.587 \times 10^{-5}$	$-6.131 \times 10^{-5}$
11.00	$-9.435 \times 10^{-6}$	$-1.154 \times 10^{-5}$	$-1.950 \times 10^{-5}$	$-4.555 \times 10^{-5}$
11.50	$-7.258 \times 10^{-6}$	$-1.062 \times 10^{-5}$	$-1.487 \times 10^{-5}$	$-3.396 \times 10^{-5}$
12.00	$-5.648 \times 10^{-6}$	$-9.168 \times 10^{-6}$	$-1.147 \times 10^{-5}$	$-2.546 \times 10^{-5}$
12.50	$-4.439 \times 10^{-6}$	$-7.651 \times 10^{-6}$	$-8.946 \times 10^{-6}$	$-1.924 \times 10^{-5}$
13.00	$-3.517 \times 10^{-6}$	$-6.266 \times 10^{-6}$	$-7.046 \times 10^{-6}$	$-1.467 \times 10^{-5}$
13.50	$-2.810 \times 10^{-6}$	$-5.081 \times 10^{-6}$	$-5.596 \times 10^{-6}$	$-1.129 \times 10^{-5}$
14.00	$-2.263 \times 10^{-6}$	$-4.104 \times 10^{-6}$	$-4.482 \times 10^{-6}$	$-8.773 \times 10^{-6}$
14.50	$-1.836 \times 10^{-6}$	$-3.313 \times 10^{-6}$	$-3.620 \times 10^{-6}$	$-6.886 \times 10^{-6}$
15.00	$-1.500 \times 10^{-6}$	$-2.680 \times 10^{-6}$	$-2.944 \times 10^{-6}$	$-5.457 \times 10^{-6}$
15.50	$-1.230 \times 10^{-6}$	$-2.176 \times 10^{-6}$	$-2.413 \times 10^{-6}$	$-4.367 \times 10^{-6}$
16.00	$-1.017 \times 10^{-6}$	$-1.775 \times 10^{-6}$	$-1.987 \times 10^{-6}$	$-3.524 \times 10^{-6}$
16.50	$-8.454 \times 10^{-7}$	$-1.456 \times 10^{-6}$	$-1.648 \times 10^{-6}$	$-2.869 \times 10^{-6}$
17.00	$-7.050 \times 10^{-7}$	$-1.201 \times 10^{-6}$	$-1.375 \times 10^{-6}$	$-2.354 \times 10^{-6}$
17.50	$-5.944 \times 10^{-7}$	$-9.960 \times 10^{-7}$	$-1.152 \times 10^{-6}$	$-1.945 \times 10^{-6}$
18.00	$-4.997 \times 10^{-7}$	$-8.312 \times 10^{-7}$	$-9.721 \times 10^{-7}$	$-1.619 \times 10^{-6}$
18.50	$-4.224 \times 10^{-7}$	$-6.973 \times 10^{-7}$	$-8.231 \times 10^{-7}$	$-1.356 \times 10^{-6}$
19.00	$-3.609 \times 10^{-7}$	$-5.886 \times 10^{-7}$	$-7.020 \times 10^{-7}$	$-1.143 \times 10^{-6}$
19.50	$-3.087 \times 10^{-7}$	$-4.990 \times 10^{-7}$	$-5.991 \times 10^{-7}$	$-9.686 \times 10^{-7}$
20.00	$-2.664 \times 10^{-7}$	$-4.256 \times 10^{-7}$	$-5.118 \times 10^{-7}$	$-8.254 \times 10^{-7}$
21.00	$-1.991 \times 10^{-7}$	$-3.136 \times 10^{-7}$	$-3.809 \times 10^{-7}$	$-6.077 \times 10^{-7}$
22.00	$-1.506 \times 10^{-7}$	$-2.354 \times 10^{-7}$	$-2.894 \times 10^{-7}$	$-4.563 \times 10^{-7}$
23.00	$-1.127 \times 10^{-7}$	$-1.795 \times 10^{-7}$	$-2.200 \times 10^{-7}$	$-3.478 \times 10^{-7}$
24.00	$-8.685 \times 10^{-8}$	$-1.392 \times 10^{-7}$	$-1.709 \times 10^{-7}$	$-2.696 \times 10^{-7}$
25.00	$-6.775 \times 10^{-8}$	$-1.092 \times 10^{-7}$	$-1.336 \times 10^{-7}$	$-2.116 \times 10^{-7}$

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