ANALYSIS OF BROADENING AND SHIFT OF 326.1 nm Cd LINE BY Ar AND Kr

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Using the Baranger nonadiabatic impact theory for different interaction potentials the values of pressure broadening and shift parameters for the 326.1 nm Cd line perturbed by Ar and Kr were calculated. Results are compared with both experimental values and those calculated in our previous papers using an adiabatic treatment.

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1. Introduction

In our previous papers [1, 2] from this laboratory results of measurements of the pressure broadening and shift of the ^{114}Cd 326.1 nm ($5\,^1S_0$–$5\,^3P_1$) intercombination line perturbed by Ar and Kr were reported. The measurements were performed for pressures of the perturbing gases below 100 Tr, and the experimental values of the pressure broadening (β) and shift (δ) coefficients were compared with those calculated in the framework of the adiabatic approximation of the Baranger [3] impact theory assuming the interaction potentials to be given in the Lennard–Jones, Morse and Czuchaj–Sienkiewicz form. In these calculations the adiabatic approximation of the Baranger theory was applied because application of the classical Lindholm–Foley phase-shift theory in the case of the Cd–Rg (Rg = Ar, Kr) systems is not quite appropriate for the following reason: Cd–Rg system in the ground state (Cd($5\,^1S_0$)+Rg($^1S_0$)) is described by one potential curve $X^1 0^+$, whereas the excited state (Cd($5\,^3P_1$)+Rg($^1S_0$)) requires two potential curves $A^3 0^+$ and $B^3 1$ for its description. The observed 326.1 nm Cd line is thus a superposition of the $A^3 0^+$–$X^1 0^+$ and $B^3 1$–$X^1 0^+$ transitions. Therefore calculations of the β and δ coefficients are carried out using the molecular potentials V_x, V_A, V_B describing the quasi-molecular states $X^1 0^+$, $A^3 0^+$, $B^3 1$, respectively.

The purpose of this paper is to calculate the values of the pressure broadening and shift coefficients for ^{114}Cd 326.1 nm ($5\,^1S_0$–$5\,^3P_1$) intercombination line

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perturbed by Ar and Kr, in the framework of the Baranger [3] impact theory, using S-matrix formalism. Recently [4] we have done such calculation for Cd 326.1 nm line perturbed by He and Ne. The calculations presented in this paper were performed using the molecular potentials described in Sec. 3.

2. Pressure broadening and shift coefficients for Cd–Ar and Cd–Kr systems

Following Baranger [3] the intensity distribution $I(\omega)$ in a broadened line can be written in the Lorentzian form

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

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

In the semiclassical case these coefficients can be written as

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

Here v denotes the relative velocity of the colliding atoms and ρ is the impact parameter. The symbol $\langle \ldots \rangle$ denotes the averaging over Maxwellian distribution of velocities, and $\{\ldots\}_{\text{Ang.Av.}}$ denotes angular averaging. S_{ii} and S_{ff} are 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 [5, 6]:

$$\{S_{ii} S_{ff}^{-1}\}_{\text{Ang.Av.}} = \sum_{\substack{m_i, m_f, \\ m_i{}', m_f{}', M}} (-1)^{2j_i + m_i + m_i{}'} \begin{pmatrix} j_f & 1 & j_i \\ m_f & M & -m_i \end{pmatrix}$$

$$\times \begin{pmatrix} j_f & 1 & j_i \\ m_f{}' & M & -m_i{}' \end{pmatrix} \langle j_i m_i | \widehat{S} | j_i m_i{}' \rangle \langle j_f m_f | \widehat{S}^{-1} | j_f m_f{}' \rangle.\tag{3}$$

We treat the collision between emitter and perturber semiclassically, using the straight line trajectory approximation. We consider the emitter to be fixed in the centre of the collisional reference frame, while the perturber moves along straight line trajectory with the constant velocity v and impact parameter ρ. The distance R between emitter and perturber at time t is thus given by $R = \sqrt{\rho^2 + v^2 t^2}$.

In the Cd–Rg (Rg = Ar, Kr) 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–Ar 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 $\{1 - S_{ii} S_{ff}^{-1}\}_{\text{Ang.Av.}}$, occurring in formula (2), is oscillating so rapidly (see Fig. 2 in [4]) that in calculations of this integral it may be replaced by its mean value [7]. Therefore we may assume that for the Cd–Rg

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

To calculate the elements of the S-matrix in Eq. (3) a system of coupled differential equations for the state amplitudes should be solved. In our calculations the quenching of the $5\,{}^3P_1$ Cd state as well as the nonadiabatic effects due to the collision-induced transitions between the fine-structure levels are neglected. Such an approach seems to be justified on the basis of the results of recent experiments on the Cd–He and Cd–Ar collisions [8, 9] which showed that both the quenching and excitation transfer cross-sections for the $5\,{}^3P_1$ Cd state are so small that they do not play any essential role in the broadening of the 326.1 nm line. Contrary to that, the nonadiabatic effects due to the rotation of the molecular axis may be very important and therefore they must be taken into account in the coupled equations. For the $5\,{}^3P_1$ state there are three coupled equations for the state amplitudes $a_{-1}(t)$, $a_0(t)$ and $a_{+1}(t)$ corresponding to three values of the quantum number m ($m = -1, 0, +1$), respectively. These coupled equations can be written in the form [4, 10, 11]

$$i\hbar\dot{a}_0(t) = a_0(t)V_B, \tag{4}$$

$$i\hbar\dot{a}_{-1}(t) = a_{-1}(t)V_1 + a_{+1}(t)fe^{+2i\phi}, \tag{5}$$

$$i\hbar\dot{a}_{+1}(t) = a_{-1}(t)fe^{-2i\phi} + a_{+1}(t)V_1. \tag{6}$$

The function f is defined by the equation

$$\langle 11|V|1-1\rangle = \langle 1-1|V|11\rangle^* = \frac{1}{2}(V_B - V_A)e^{-2i\phi} = fe^{-2i\phi}, \tag{7}$$

where

$$\langle 10|V|10\rangle = V_B, \tag{8}$$

$$\langle 11|V|11\rangle = \langle 1-1|V|1-1\rangle = \frac{1}{2}(V_A + V_B) = V_1. \tag{9}$$

For the Cd atom in its ground state $5\,{}^1S_0$ perturbed by rare gas atom the state-amplitude $a'_0(t)$ fulfils the single equation

$$i\hbar\dot{a}'_0(t) = a'_0(t)V_X, \tag{10}$$

where

$$\langle 00|V|00\rangle = V_X. \tag{11}$$

3. Interaction potentials for the Cd–Ar and Cd–Kr systems

For the Cd–Ar and Cd–Kr systems there exist theoretical potential curves calculated from the pseudopotentials method [12]. For these systems one can also use model potentials like those of the Morse and Lennard–Jones forms. The spectroscopic constants corresponding to such potentials have been recently measured by Bobkowski et al. [13], and Czajkowski et al. [14, 15].

3.1. Pseudopotential method

Czuchaj and Sienkiewicz [12] calculated the adiabatic potentials for the Cd–Rg systems (Rg = Ar, Kr, Xe) developing modified version for semiempirical pseudopotential suggested originally by Baylis [16]. 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. This pseudopotential includes three effects. The first one is the effect of incomplete screening of the nuclear charge due to the core electrons. The second one is the Pauli repulsion (antisymmetry effect due to the Pauli principle). The third effect is the polarization effect resulting from interaction between induced dipole moment of Rg atom, core of Cd and its valence electrons.

These potentials were calculated in the range of the internuclear distances $4.0 \leq R \leq 50.0$ a.u. using different step sizes. Hereafter such potentials will be

TABLE I

The experimental and theoretical values of the pressure broadening β and shift δ coefficients (in units 10^{-20} cm^{-1}/(atom · cm^{-3})) for the ^{114}Cd 326.1 nm line perturbed by argon. Numbers in parenthesis represent the standard deviation of the least squares fit. Notations are explained in the text.

	β		δ	
	adiabatic [1]	nonadiabatic	adiabatic [1]	nonadiabatic
C–S	1.75	1.50	−0.59	−0.51
Morse	1.42	0.98	−0.08	−0.01
L–J	1.00	0.64	−0.33	−0.11
Exp [1]	1.04(0.02)		−0.29(0.03)	

TABLE II

The experimental and theoretical values of the pressure broadening β and shift δ coefficients (in units 10^{-20} cm^{-1}/(atom · cm^{-3})) for the ^{114}Cd 326.1 nm line perturbed by krypton. Numbers in parenthesis represent the standard deviation of the least squares fit. Notations are explained in the text.

	β		δ	
	adiabatic [2]	nonadiabatic	adiabatic [2]	nonadiabatic
C–S	1.54	1.41	−0.69	−0.57
Morse	1.02	0.77	−0.11	−0.11
L–J	0.48	0.47	0.06	−0.01
Exp [2]	1.00(0.03)		−0.27(0.03)	

denoted as C–S. Results of calculations using C–S potentials for the Cd–Ar and Cd–Kr system are presented in Tables I and II respectively.

3.2. Morse potential

In the present study we assumed a Morse potential in the form

$$V(R) = D_e \left[e^{-2\kappa(R-R_e)} - 2e^{-\kappa(R-R_e)} \right], \tag{12}$$

where

$$\kappa = \sqrt{\frac{8\pi^2 c\mu\omega_e x_e}{h}}, \tag{13}$$

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

The constants $(D_e, R_e, \omega_e x_e)$ were determined in spectroscopic investigation of the Cd–Ar and Cd–Kr molecules in free-jet supersonic expansion molecular beam in Refs. [14–16].

The most complete set of experimental results for the Cd–Rg systems (Rg = Ne, Ar, Kr, Xe) is collected by Czajkowski et al. [16] who has also corrected the previous analysis for the various states given in previous papers. For the Cd–Ar and Cd–Kr systems, we used the spectroscopic constants $(D_e, R_e, \omega_e x_e)$ given in [16]. The values of the β and δ parameters for the Cd–Ar and Cd–Kr systems calculated with the potential (12) are listed in Tables I and II (marked Morse).

3.3. Lennard–Jones potential

In our previous papers [1,2] the experimental values of the pressure broadening β and shift δ coefficients for the Cd $\lambda = 326.1$ nm line perturbed by Ar and Kr were compared with values calculated on the basis of the Lennard–Jones potential. We found good agreement between experimental and calculated values. The Lennard–Jones potential is given by the formula

$$V(R) = -\frac{C_6}{R^6} + \frac{C_{12}}{R^{12}}, \tag{14}$$

where C_6 and C_{12} are force constants.

Let us note that the Lennard–Jones potential may be rewritten in an alternative form

$$V(R) = D_e \left[-2 \left(\frac{R_e}{R} \right)^6 + \left(\frac{R_e}{R} \right)^{12} \right]. \tag{15}$$

The appropriate force constants are $C_6 = 2D_e R_e^6$ and $C_{12} = D_e R_e^{12}$. In this paper we used the potential (15) with the values of D_e and R_e for the $X^1 0^+$, $A^3 0^+$ and $B^3 1$ states the same as for the Morse potential (see previous subsection). Such a potential hereafter will be denoted as L–J. Results of calculations for the Cd–Ar system are presented in Table I, and for Cd–Kr system in Table II.

4. Results and discussion

The calculations of the pressure broadening β and shift δ coefficients were performed assuming that the averaging over the Maxwellian distribution of velocities may be replaced by putting the mean value of the relative emitter–perturber velocity into relevant equations. This approximation has been used by many authors and usually it does not lead to significant errors.

The differential equations (4), (5), (6) and (10) 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 ρ values changing in the range of a potential. The lower limit ρ_{min} was about 6.00 a.u., the upper limit ρ_{max} was 50.00 a.u. We have checked that the values of ρ greater than $\rho_{max} = 50$ a.u. had negligible influence on the value of the integral (2). The calculations of the ρ-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 values of ρ less than ρ_{min}, where the S-matrix values are not defined, we used the Anderson approximation [7].

Tables I and II show the values of the pressure broadening β and shift δ coefficients for the ^{114}Cd 326.1 nm line perturbed by argon and krypton, respectively.

In Table I the results of calculation for C–S, Morse and L–J potentials are presented for Cd–Ar system. As can be seen from the table, the best agreement between the calculated and experimental values of the β and δ coefficients is obtained in the case of adiabatic calculations for L–J potential. Though for the other potentials the nonadiabatic calculations gave the better agreement between theoretical and experimental results, the obtained improvement is not satisfactory yet, especially for the shift coefficients δ.

Results of calculations presented in Table II were obtained for C–S, Morse and L–J potentials for Cd–Kr system. The best agreement takes place for the adiabatic case with Morse potential.

As can be seen from Tables I and II the inclusion of the rotation of the interatomic axis leads to better agreement of calculated values of β and δ with experimental results for Cd–Ar and Cd–Kr systems although the improvement in the agreement is not so impressive as that obtained for Cd–He and Cd–Ne systems in [4]. The reason why some disagreements between theoretical and experimental values of β and δ still remain, seems to be connected with the form of chosen interatomic potentials for Cd–Rg. For low densities C–S potentials used in the present analysis were constructed for small interaction distances. On the other hand, in the case of Cd–Ar and Cd–Kr systems the transition from the Hund case "c" to Hund case "a" occurs at relatively large distances which are essential and which are not encompassed by C–S potentials. Therefore it seems that in order to improve theoretical results for Cd–Ar and Cd–Kr systems we would have to construct other types of the interatomic potential. In conclusion, we should emphasize that the knowledge of very precise experimental values of the width and shift parameters may provide a critical test for accuracy of theoretical potentials at large interatomic separations.

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