Quasimolecular absorption and emission near the forbidden atomic line \( \text{Cd} \left( 5^3\mathrm{P}_2 - 5^1\mathrm{S}_0 \right) \) in \( \text{Cd} + \text{Ar} \) and \( \text{Kr} \) collisions

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Abstract. We report on the theoretical study of quasimolecular absorption and emission near the forbidden atomic line \( \text{Cd} \left( 5^3\mathrm{P}_2 - 5^1\mathrm{S}_0 \right) \) in a mixture of cadmium vapor with inert gases (argon and krypton). By using the semiempirical method of quasimolecular term analysis and available experimental potential curves the interaction potentials of the excited atoms \( \text{Cd}^* + \text{Kr} \) and \( \text{Cd}^* + \text{Ar} \) and the probabilities of the radiative transitions were calculated. Based on them the processes of quasimolecular absorption and emission in mixtures of \( \text{Cd} \) with \( \text{Ar} \) and \( \text{Kr} \) atoms were considered and the absorption coefficients and emission spectra were calculated. Also the rate constants of radiative decay of the metastable state of \( \text{Cd} \) atoms in collisions with \( \text{Kr} \) and \( \text{Ar} \) were calculated.

1. Introduction

In this paper the collision-induced absorption and emission near the forbidden line \( \text{Cd} \left( 5^1\mathrm{S}_0 - 5^3\mathrm{P}_2 \right) \) in mixtures of cadmium vapor with krypton and argon are investigated theoretically.

The calculation of spectral characteristics of these processes requires that the potential curves of the interaction of atoms in the ground and the excited states and the square of the dipole moment of the transitions between these states as a function of the interatomic distance be known. Therefore at first the interaction potentials for \( \text{Cd} \left( 5^3\mathrm{P}_2 \right) \) - RG in \( \Omega = 0,1,2 \) states and the probabilities of qasimolecular radiative transitions \( 1\left( ^3\mathrm{P}_2 \right) - 0\left( ^1\mathrm{S}_0 \right) \) were obtained from the available experimental interaction potentials for \( 1\left( ^3\mathrm{P}_2 \right) \) and \( 0\left( ^1\mathrm{S}_0 \right) \) states \([1-5]\) by making use of the semiempirical method of quasimolecular term analysis \([6]\). Based on these results the processes of quasimolecular absorption and emission in \( \text{Ar} \) and \( \text{Kr} \) in collisions with \( \text{Cd} \) atoms were considered and the absorption coefficients and emission spectra were calculated.

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2. Potential curves and probabilities of quasi-molecular radiative transitions

To calculate the potentials of interatomic interaction and the probabilities of quasi-molecular radiative transitions we used the effective Hamiltonian method [7] in the formulation [8]. The nonzero matrix elements of the effective Hamiltonian in the basis $|1^3P_P^\Omega\rangle$ of diabatic quasimolecular wave functions of coupling case $c$, which are the products of the atomic wave functions

$$
|1^3P_P^\Omega\rangle = \text{Cd}(1^3P_P^\Omega)|1^3P_P^\Omega\rangle_{ic}^{at} [R G(1^3S_0)]
$$

(1)

The potential curves for the excited states were obtained within the framework of the semiempirical method of quasimolecular term analysis [6]. The method is based on the comparison of four eigenvalues of the matrix of the effective Hamiltonian with interaction potentials for the states $1^1(^3P), 1^1(^1P), 0^+ (^3P)$ and $0^+ (^1P)$ reconstructed from experimental data. The point is, all matrix elements of the effective Hamiltonian can be expressed through atomic constants and the quantities $1^3H_d(R)$, $1^3H_a(R)$, which represent the potentials of the interaction in $1^3\Sigma$ and $1^3\Pi$ states without regard for the spin–orbit interaction in the Cd atom. Thus the functions $1^3H_d(R)$, $1^3H_a(R)$ can be determined from the available experimental potentials for four states and then the potential curves for the remaining four states can be found from these functions by diagonalization of the matrix of the effective Hamiltonian.

Using the quantities $1^3H_d(R)$ and $1^3H_a(R)$ calculated, the probability $\Gamma(1^1(^3P), R)$ of the quasimolecular radiative transitions $1^1(^3P) \rightarrow 0^+ (1^3S_0)$ per unit time at a fixed interatomic distance $R$ can be determined. The adiabatic quasimolecular wave functions $\Omega(1^3P)$ (the eigenfunctions of the effective Hamiltonian) can be presented as linear combinations of the diabatic functions. In particular,

$$
1^1(^3P) = c_1(R)1^1(^3P_{1e}) + c_2(R)1^1(^3P_{2e}) + c_3(R)1^1(^3P_{3e}),
$$

(2)

where the coefficients $c_i(R)$ are determined by diagonalizing the matrix of the effective Hamiltonian. The atomic wave functions for the intermediate coupling case in turn can be presented as linear combination of the wave functions for the $LS$ coupling case with amplitudes $a$ and $b$:

$$
\text{Cd}(1^3P^\Omega)|1^3P^\Omega\rangle_{ic}^{at} = a\text{Cd}(1^3P^\Omega)|1^3P^\Omega\rangle_{LS}^{at} + b\text{Cd}(1^3P^\Omega)|1^3P^\Omega\rangle_{LS}^{at},
$$

(3)

$$
\text{Cd}(1^3P^\Omega)|1^3P^\Omega\rangle_{ic}^{at} = -b\text{Cd}(1^3P^\Omega)|1^3P^\Omega\rangle_{LS}^{at} + a\text{Cd}(1^3P^\Omega)|1^3P^\Omega\rangle_{LS}^{at}.
$$

(4)

In the calculations the approximate values of the amplitudes $a = 0.998$ and $b = 0.062$ were used, which, as in [9], were determined from the energies of atomic levels using the semiempirical method of the atomic spectra analysis [10].

To calculate the probabilities $\Gamma(\Omega(1^3P), R)$ of the quasimolecular radiative transitions in adiabatic wave functions we isolated the contribution from the diabatic functions $|1^3P_{0e}^\Omega\rangle$ and $|1^3P_{1e}^\Omega\rangle$, since in
the diabatic molecular basis \( |1^3P_1\Omega_{L_S}\rangle \) corresponding to the \( LS \) coupling case, the dipole moments of the transitions to the ground state are nonzeros only for the \( 1^3P_0 0^1S \) and \( 1^3P_1 0^1S \) states. In particular, 
\[
\langle 1^3P_1 0^1S \mid d \mid 0^1S_0 0 \rangle = ac_1 - bc_3. \tag{5}
\]

The dipole moment \( \langle 1^3P_1 0^1S \mid d \mid 0^1S_0 0 \rangle \) is associated with the dipole moment \( \langle 0^3P_0 0^1S \mid d \mid 0^1S_0 0 \rangle \) of an observed atomic transition. Thus the probability \( \Gamma (1^3P_2, R) \) of the quasi-molecular radiative transition can be expressed in terms of the probability \( \Gamma (0^3P_1) \) and frequency \( \omega (0^3P_1) \) of the atomic intersystem crossing transition and the calculated amplitudes \( a, b, c_1, c_3 \).
\[
\Gamma (1^3P_2, R) = \Gamma (0^3P_1) \left( \frac{\omega (1^3P_2, R)}{\omega (0^3P_1)} \right)^3 \left( \frac{a}{b} \frac{c_1}{c_3} \right)^2. \tag{6}
\]

Figures 1 and 2 display calculated values of reduced widths
\[
\gamma (1^3P_2, R) = \frac{\Gamma (1^3P_2, R)}{\Gamma (0^3P_1)} \left( \frac{\omega (0^3P_1)}{\omega (1^3P_2, R)} \right)^3. \tag{7}
\]

They are almost independent of the quasi-molecular ground state, which affects the magnitude of \( \omega (R) \), and characterize the square of the ratio of the dipole moment of the quasi-molecular transition \( 1^3P_2 - 0^1S_0 \) to the dipole moment of the \( 0^3P_1 - 0^1S_0 \) atomic transition.

The interaction potentials for the ground \( U_0 \) and excited \( U^* \) states and the difference potentials \( \Delta U \) are shown also in Figures 1 and 2. For the ground state the potentials determined in studies [1, 6] have been used.

3. Quasi-molecular absorption and emission near the forbidden line \( \text{Cd} \left( 5^1S_0 - 5^3P_2 \right) \)

For a mixture of cadmium vapor with inert gases, the optical absorption and emission spectrum near the forbidden line \( \text{Cd} \left( 5^1S_0 - 5^3P_2 \right) \) are determined by the processes
\[
\begin{align*}
\text{Cd} \left( 5^5s^2 1^3S_0 \right) + \text{RG} + h\omega &\rightarrow \begin{cases} 
\text{Cd} \left( 5^5s5p^3P_2 \right) + \text{RG}, \\
\text{CdRG} \left( 1^3P_2 \right) 
\end{cases} \quad \text{(absorption)} \tag{8} \\
\text{Cd} \left( 5^5s5p^3P_2 \right) + \text{RG} &\rightarrow \begin{cases} 
\text{Cd} \left( 5^5s^2 1^3S_0 \right) + \text{RG} + h\omega, \\
\text{CdRG} \left( X^1\Sigma^+ \right) + h\omega 
\end{cases} \quad \text{(emission)}
\end{align*}
\]
and
CdRG \left(X^1\Sigma\right) + h\omega \rightarrow \begin{cases} 
\text{Cd} \left(5s^5p^3P_z\right) + \text{RG}, \\
\text{CdRG} \left(1^3P_z\right) 
\end{cases} \quad \text{(absorption)}
\tag{9}

CdRG \left(1^3P_z\right) \rightarrow \begin{cases} 
\text{Cd} \left(5s^2P_n\right) + \text{RG} + h\omega, \\
\text{CdRG} \left(X^1\Sigma\right) + h\omega 
\end{cases} \quad \text{(emission)}

The first of them correspond to free-free and free-bound transitions and the second corresponds to bound-free and bound-bound transitions.

The spectral distribution of absorption coefficient of a mixture of cadmium vapor with an inert gas in the short-wavelength (with respect to the forbidden atomic line) spectral region, where the role of bound-bound transitions is insignificant, and the spectral distribution of photons emitted in the processes (10) and (11) normalized by the condition $\int I(T,\Delta \omega)d\Delta \omega = 1$, are determined within the framework of the well-known quasi-static approximation [11].
22* 0 4, exp ,8 RR C CC C  absRR U RIT kTdUR = /g1/g9πΓΔω = −/g2/g10/g2/g10Δ /g3/g11

(10)

where \( \lambda \) is the wavelength of quasi-molecular absorption, \( T \) is the temperature of the gas mixture, \( k \) is the Boltzmann constant, \( \frac{g^*}{g_0} = 2 \) is the ratio of the statistic weights of the electron states \( ^1P \) and \( ^3P \), \( U_0 \) and \( U^* \) are the interaction potential for atoms on the ground and excited states respectively, \( \Delta U \) is the difference potential, \( \Gamma(R) \) is the probability of the quasi-molecular radiative transition \( ^1P \rightarrow \Sigma \), \( \Gamma_0 \) is the Condon point, and the quantity

\[
K(T) = \frac{2}{5} \pi R_c \Gamma(R) \exp \left( -\frac{U^*(R)}{kT} \right) R^2 dR
\]

characterizes the integrated (over the spectrum) rate constant of radiative decay of the metastable state.

The values of \( K(T) \) for \( T = 300 \) K and \( T = 700 \) K are presented in Table 1.

**Table 1.** Integrated (over the spectrum) rate constants \( K(T) \) (in \( 10^{18} \) cm\(^3\)s\(^{-1}\)) of radiative decay of the metastable state in the processes (8) and (9) for CdKr and CdAr

| T, K   | 300  | 700  |
|--------|------|------|
| CdKr   | 2.4  | 3.3  |
| CdAr   | 1.1  | 1.9  |

The results of calculations of the spectral distributions of the absorption coefficients \( K_{abs}(T,\Delta\omega) \) and emission spectrum of mixtures of cadmium vapor with krypton and argon for \( T = 300 \) K and \( T = 700 \) K are presented in the figures 3 and 4.

As follows from the calculation results the position of the maximum of the spectral distribution of the absorption coefficient is shifted toward the shorter wavelengths slowly enough and the magnitude of the maximum decreases with increasing temperature. The width of the spectral distribution grows with increasing temperature. The maximum of the emission spectrum moves also rather slowly to the short-wavelength side with increasing temperature, whereas the distribution is broadened.
Figure 3. The spectral distributions of the absorption coefficients of mixtures of Cd vapor with Kr and Ar for $T = 300$ K and $T = 700$ K

Figure 4. The normalized spectral distribution for the quasimolecular emission of mixtures of Cd vapor with Kr and Ar for $T = 300$ K and $T = 700$ K

4. Conclusion

The emission spectra represent continuous bands shifted to the short-wavelength region with respect to the position of the forbidden atomic line. For $T \geq 300$ K the depth of the potential well of the state $1\left( ^{3}P_{2} \right)$ is smaller than $kT$. Therefore the relative population of bound states is small and states of continuum are preferentially populated. The major contribution to the emission of mixtures of cadmium vapor with Kr and Ar near the forbidden atomic line is made by quasi-molecular radiative transitions in the region of the nearest approach of atoms in the collision process, i.e. the spectrum is formed by the radiative-collisional quenching of the metastable state.

Absorption spectra also represents continuous bands. As follows from the behavior of the interaction potentials and the reduced width the process of absorption is most efficient in the short-wavelength (with respect to the forbidden line) spectral region. The main result of the process of the absorption is the formation of metastable atoms Cd($^{3}P_{2}$) (long-lived excited molecules CdRG in the state $1\left( ^{3}P_{2} \right)$ can be formed only for relatively small shifts), therefore the processes of optical absorption lead to selective population of the metastable state Cd($^{3}P_{2}$).

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