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Cross Sections for Transitions between Fine Structure Components of Second Group Excited Atoms Induced by Collisions with Noble Gas Atoms

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Cross sections of the transition $^3P_1 \rightarrow {}^3P_0$ for the atoms Zn, Cd, Hg upon collisions with inert gas atoms are calculated. It is shown that the transitions between fine structure components induced by nonadiabatic interaction are due to rotation of the molecule. A numerical estimation of the cross sections is performed.

Es werden Wirkungsquerschnitte für den Übergang $^3P_1 \rightarrow {}^3P_0$ für die Atome Zn, Cd, Hg bei Stößen mit Edelgasatomen berechnet. Es wird gezeigt, daß die Übergänge zwischen Feinstrukturkomponenten, induziert durch nicht-adiabatische Wechselwirkung, durch Rotation des Moleküls bewirkt werden. Es wird eine numerische Abschätzung der Wirkungsquerschnitte durchgeführt.

Calcul des sections efficaces pour la transition $^3P_1 \rightarrow {}^3P_0$ dans les atomes Zn, Cd, Hg par collision avec des atomes de gaz rare. On montre que les transitions entre les composantes de structure fine induites par interaction non adiabatique sont dues à la rotation de la molécule. Estimation numérique des sections efficaces.

Introduction

Lately there have been performed some calculations of the transitions cross sections between fine structure components of alkali metals in P-state for different collision pairs (Na*–Na, Na*–Ar, K*–K, K*–Ar, Cs*–He etc. [1—3]). It has been shown that the exchange forces play an important role in nonadiabatic transition processes and cross sections close to the experimental ones were obtained.

This paper considers the reactions of the type:

$$\mathrm{M}^*(^3P_1) + \mathrm{X}(^1S_0) \rightarrow \mathrm{M}^*(^3P_0) + \mathrm{X}(^1S_0) + \Delta\varepsilon\,. \qquad (1)$$

The electron excitation energy $\Delta\varepsilon$ is transferred in kinetic energy of colliding pairs.

M denotes any of the II group P-state elements of the periodical table (Zn, Cd, Hg). X is noble gas atom.

In the series Zn, Cd, Hg the spin-orbital splitting $\Delta\varepsilon$ changes from 190 cm^{-1} to 1767 cm^{-1}. This splitting is so large that Massey parameter $\xi = \frac{\Delta\varepsilon}{\hbar\alpha V}$ where $1/\alpha$ is the effective interaction distance, far exceeds unity. This leads to exponentially small transition probabilities.

The mechanism of the nonadiabatic transition in (1) will be shown to be different from that of transitions between components of the doublet of alkali metals.

A calculation of the transition cross section for the reaction (1) will be done in the following.

The Hamiltonian of the rotating system with fixed internuclear distance is:

$$H = H_{\mathrm{M}} + H_{\mathrm{X}} + V + V_{SO} + \omega(L_x + S_x) + V_R \tag{2}$$

where H_{M} and H_{X} are the Hamiltonians of atoms M and X.

V is the interaction between the atoms X and M.

V_{SO} is the operator of the spin-orbital coupling.

L and S are the orbital and spin momenta of electrons. The x axis is taken to be directed along the angular velocity vector ω, whose direction is preserved in our approximation. The last two terms are so-called nonadiabatic corrections, which are excluded from the Schrodinger equation in the Born-Oppenheimer approximation. The first of two terms in (2) is due to the rotation of the molecular axis and the last is due to the radial movement of the colliding atomic pair. From the selection rules for electronic transitions of a quasimolecule it can easily be found that only the term $\omega(L_x + S_x)$ can induce transitions $\Delta\Omega = \pm 1$.

The scheme of calculation is as follows.

Taking as a basis the eigenfunctions of Hamiltonian [1]:

$$H_0 = H_{\mathrm{M}} + H_{\mathrm{X}} + V_{SO} \tag{3}$$

we determine the eigenvalues and eigenfunctions of the adiabatic Hamiltonians:

$$H_1 = H_0 + V\,. \tag{4}$$

These molecular eigenfunctions are used to calculate the transition probability.

The Calculation of Wave Functions and Quasimolecule Energy Terms for the Pair M*-X

The eigenfunctions of the operator H_0 are:

$$\begin{aligned}
\varphi_1 &= |\, j = 0, m_j = 0 > &&= \frac{1}{\sqrt{3}}(\psi_{1,-1}\chi_{1,1} + \psi_{1,1}\chi_{1,-1} - \psi_{1,0}\chi_{1,0}) \\
\varphi_2 &= |\, j = 1, m_j = 0 > &&= \frac{1}{\sqrt{2}}(\psi_{1,1}\chi_{1,-1} - \psi_{1,-1}\chi_{1,1}) \\
\varphi_3 &= |\, j = 1, m_j = 1 > &&= \frac{1}{\sqrt{2}}(\psi_{1,1}\chi_{1,0} - \psi_{1,0}\chi_{1,1}) \\
\varphi_4 &= |\, j = 1, m_j = -1 > &&= -\frac{1}{\sqrt{2}}(\psi_{1,-1}\chi_{1,0} - \psi_{1,0}\chi_{1,-1}) \\
\varphi_5 &= |\, j = 2, m_j = 0 > &&= \sqrt{\frac{2}{3}}\psi_{1,0}\chi_{1,0} + \sqrt{\frac{1}{6}}(\psi_{1,-1}\chi_{1,1} + \psi_{1,1}\chi_{1,-1}) \\
\varphi_6 &= |\, j = 2, m_j = 1 > &&= \sqrt{\frac{1}{2}}(\psi_{1,1}\chi_{1,0} + \psi_{1,0}\chi_{1,1}) \qquad (5) \\
\varphi_7 &= |\, j = 2, m_j = -1 > &&= \sqrt{\frac{1}{2}}(\psi_{1,-1}\chi_{1,0} + \psi_{1,0}\chi_{1,-1}) \\
\varphi_9 &= |\, j = 2, m_j = 2 > &&= \psi_{1,1}\chi_{1,1} \\
\varphi_8 &= |\, j = 2, m_j = -2 > &&= \psi_{1,-1}\chi_{1,-1}
\end{aligned}$$

where $\chi_{1,k}$ is the spin-function with $S = 1$, $S_z = k$.

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* It is assumed that the derivation from L-S type coupling can be neglected.

Of the off-diagonal elements of the matrix H_1 in the φ_i basis only H_{15} and H_{36} are different from zero. We therefore form the following linear combinations:

$$\begin{aligned} &\Psi_1 = b_1^1\,\varphi_1 + b_5^1\,\varphi_5 \qquad &&\Psi_3 = b_3^1\,\varphi_3 + b_6^1\,\varphi_6 \qquad &&\Psi_5 = \varphi_2 \\ &\Psi_2 = b_1^2\,\varphi_1 + b_5^2\,\varphi_5 \qquad &&\Psi_4 = b_3^2\,\varphi_3 + b_6^2\,\varphi_6 \qquad &&\Psi_6 = \varphi_8\,. \end{aligned} \tag{6}$$

The energies corresponding to functions Ψ_i and coefficients b_μ^ν are found by conventional methods. Denoting:

$$H\sigma = \langle \psi_{1,0} \,|\, H \,|\, \psi_{1,0} \rangle\;; \qquad H\pi = \langle \psi_{1,1} \,|\, H \,|\, \psi_{1,1} \rangle \tag{7}$$

we can write the adiabatic energies of the Hamiltonian H as:

$$\begin{aligned} E_1 &= \frac{H\sigma + H\pi}{2} + \frac{3\Delta\varepsilon}{2} + \frac{1}{2}\sqrt{9\Delta\varepsilon^2 - 2(H\pi - H\sigma)\,\Delta\varepsilon + (H\pi - H\varepsilon)^2} \\ E_2 &= \frac{H\sigma + H\pi}{2} + \frac{3\Delta\varepsilon}{2} - \frac{1}{2}\sqrt{9\Delta\varepsilon^2 - 2(H\pi - H\sigma)\,\Delta\varepsilon + (H\pi - H\sigma)^2} \\ E_{3,4} &= \frac{H\sigma + H\pi}{2} + 2\Delta\varepsilon \pm \frac{1}{2}\sqrt{4\Delta\varepsilon^2 + (H\pi - H\sigma)^2} \\ E_5 &= H\pi + \Delta\varepsilon; \qquad\qquad E\sigma = H\pi + 3\Delta\varepsilon\,. \end{aligned} \tag{8}$$

In general the functions $H\sigma$ and $H\pi$ change non-monotonously with the internuclear distance R. When R is large enough the main contribution is due to polarization, so that $H\sigma \ll H\pi < 0$. At small distances the exchange interaction of the pair M*–X leads to repulsion, so that $H\sigma \gg H\pi > 0$. For the two extreme cases the correlation of energy terms is shown in Fig. 1, 2.

From Figs. 1 and 2 it is seen that the transition $\Omega = 1 \rightarrow \Omega = 0$ followes quite different mechanisms in the two cases. If $H\pi \ll H\sigma < 0$ the rotation will induce transitions between the energy terms 1 and 0^-. If in this case $H\sigma - H\pi \gg \Delta\varepsilon$ these terms go to the same limiting term $^3\Sigma^+$.

If $H\sigma \gg H\pi > 0$ the rotation causes transitions between energy terms of the same symmetry. The distance between such terms, however, depends only slightly on R. Between the converging terms 0^+ and 0^- there are no transitions, because the

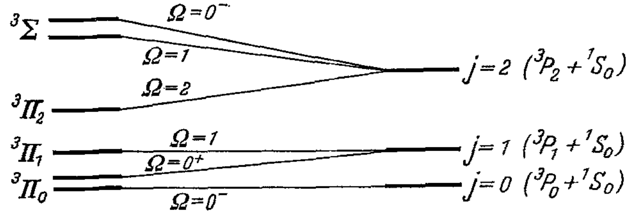

Fig. 1. Electronic Terms of a System M* –X for the case $H_\sigma \ll H_\pi < 0$

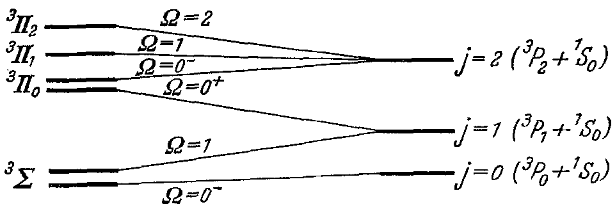

Fig. 2. Electronic Terms of a System M* –X for the case $H_\sigma \ll H_\pi < 0$

"parity" (+) and (−) (different symmetry with respect to the reflection in the rotation plane) remains a good quantum number even when rotation is taken into account. Here we shall consider only the second case. The choise of this case in supported by the fact that experimental cross sections for the processes (1) are found to be very small [4].

The splitting between the energy terms 1 and 0^- in case $H\sigma \gg H\pi > 0$ is the following:

$$\Delta E = \frac{\Delta\varepsilon}{2} + \frac{1}{2}\sqrt{9\,\Delta\varepsilon^2 + 2\,H\sigma\,\Delta\varepsilon + H\sigma^2} - \frac{1}{2}\sqrt{4\,\Delta\varepsilon^2 + H\sigma^2} \tag{9}$$

The wave functions of O and 1 states are:

$$\begin{aligned} \Psi_2(0^-) &= b_1^2\,\varphi_1 + b_5^2\,\varphi_5 \\ \Psi_4(1) &= b_3^2\,\varphi_3 + b_6^2\,\varphi_6 \end{aligned} \tag{10}$$

where

$$b_5^2 = \frac{1}{\sqrt{2}}\left[1 - \frac{\frac{1}{3}H\sigma + 3\Delta\varepsilon}{(9\,\Delta\varepsilon^2 + 2\,H\sigma\,\Delta\varepsilon + H\sigma^2)^{1/2}}\right]^{1/2};\; b_6^2 = \frac{1}{\sqrt{2}}\left[1 - \frac{2\,\Delta\varepsilon}{(4\,\Delta\varepsilon^2 + H\sigma^2)^{1/2}}\right]^{1/2}$$

The matrix element V_{24} of the transition operator is:

$$\begin{aligned} V_{24}(R) &= \langle\Psi_2\,|\,\omega(L_x + S_x)\,|\,\Psi_4\rangle \\ &= \frac{3\omega}{2\sqrt{6}}\left[1 - \frac{\frac{1}{3}\,H\sigma + 3\,\Delta\varepsilon}{(9\,\Delta\varepsilon^2 + 2\,H\sigma\,\Delta\varepsilon + H\,\sigma^2)^{1/2}}\right]^{1/2}\left[1 - \frac{2\Delta\varepsilon}{(H\sigma^2 + 4\,\Delta\varepsilon^2)^{1/2}}\right]^{1/2} \end{aligned} \tag{11}$$

where $\omega = \frac{u}{2\,\mu\,\mathrm{R}^2}$ and u is the relative angular momentum, which remains constant.

As the splitting between the energy terms 1 and 0^- is large and the perturbation is small (the frequency of rotation ω is small) one can calculate the transition probability to the first order of the perturbation theory. An additional simplification emerges from the application of semiclassical approximation after which we introduce a certain trajectory $R = R(T)$.

The formula for transition probability is:

$$P = \left|\frac{i}{\hbar}\int\limits_{-\infty}^{+\infty} V_{2\mu}(R)\,\exp\left[\frac{i}{\hbar}\int^{t}\Delta E(t')\,dt'\right]dt\,\right|^2 \tag{12}$$

Let us now make use of the fact that the exchange interaction decreases approximately exponentially. To find singularity points of the integrand one can take $H\sigma = A\,\exp\,(-\alpha\,R)$, where the dependence of A upon R can be neglected as compared with the exponential function. Introducting the variable $u = \alpha(R - R_0)$, where $A(R_0)\,\exp\,(-\alpha\,R_0) = \Delta\varepsilon$, the integral in the formula (12) is:

$$I = \frac{3}{\sqrt{6}}\int\limits_{-\infty}^{+\infty} \omega(u)\,f_1(u)\,f_2(u)\,\exp\left[\frac{i\Delta\varepsilon}{2\alpha}\int^{u}\Delta E(u')\,\frac{du'}{V_R}\right]\frac{du}{\alpha V_R} \tag{13}$$

where V_R is the radial velocity $V_R = V\infty\left(1 - \frac{\varrho^2}{R_0^2}\right)^{1/2}$

$$f_1(u) = \left[1 - \frac{2}{[4 + \exp(-2u)]^{1/2}}\right]^{1/2};\; f_2(u) = \left[1 - \frac{3 + \frac{1}{3}\exp(-u)}{[9 + 2\exp(-u) + \exp(-2u)]^{1/2}}\right]^{1/2}$$

$$\Delta E(u) = 1 + \sqrt{9 + \exp(-2u) + 2\exp(-u)} - \sqrt{4 + \exp(-2u)} \tag{14}$$

Integral I is calculated by the Landau method — by displacing the path of integration to the complex plane to make the integrand exponentially small.

The singularity points (namely the polar points of branching) are found from the equations:

$$9 + 2\exp(-u) + \exp(-2u) = 0 \text{ roots } u = \mu_1 \pm 2k\pi i;\ u = \mu_2 \pm 2k\pi i \tag{15}$$

$$4 + \exp(-2u) = 0 \qquad \text{roots } u = \mu_3 \pm 2k\pi i;\ u = \mu_4 \pm 2k\pi i\,.$$

The main contributions to the integral are due to such parts of the contour who are near the branching points μ_1 and μ_3, since exponential functions in integrand decrease rapidly when one moves away from μ_1 and μ_3.

Because of that we take into account only the contributions from the singularity points μ_1 and μ_3 which are nearest to the real axis. The integration contour is given in Fig. 3. The next two singularity points give a smaller contribution to the integral. In such way we have obtained two integrals along the contours C_1 and C_2, which are transformed into the Γ-functions.

$$I = I_1 + I_2$$

$$\begin{aligned} I_1 &= \frac{3\omega}{2\sqrt{6}\,2^{1/4}}\,\frac{\exp(-i\alpha 0)}{\alpha V}\int_{C_1}\frac{\exp[i\lambda(A_1 + B_1 u - B_1\mu_3)]}{(u-\mu_3)^{1/4}}\,du \\ &= \frac{\sqrt{3}\,\omega\,\Gamma(\frac{3}{4})}{2^{5/4}(\lambda\,|B_1|)^{3/4}}\,\frac{\exp[i(\lambda A_1 - \alpha 0 - \pi/4 - 3\gamma_1/4)]}{\alpha V}\,; \end{aligned} \tag{16}$$

where

$$\lambda = \frac{\Delta\varepsilon}{2V\alpha}\,;\ \alpha_0 = 1{,}3;\ A_1 = 1{,}8 + 4i;$$

$$\gamma_1 = 0{,}2;\quad B_1 = 3{,}4 - 0{,}8i;\ I_1 = |\,I_1\,|\exp(i\psi_1)$$

$$|\,I_1\,|^2 = 0{,}1\,\frac{\omega_2\exp(-2\lambda\,Im\,A_1)}{\alpha^2\,V^2\,\lambda^{3/2}}\ ,\ \psi_1 = 1{,}8\,\lambda - 1{,}1 - \pi/4\,.$$

For I_2 we get:

$$\begin{aligned} I_2 &= 1{,}25\,\frac{3^{1/4}}{2^{3/8}}\,\frac{\omega}{\alpha V}\exp[i(\lambda A_2 - \beta_0)]\int_{C_2}\frac{\exp[i\lambda B_2(u-\mu_3)]}{(u-\mu_3)^{1/4}}\,du \\ &= \frac{1{,}7\,\Gamma(\frac{3}{4})}{(\lambda\,|B_2|)^{3/4}}\,\frac{\omega}{\alpha V}\exp\left[-\lambda A_2 - i\beta_0 + \frac{3i\gamma_2}{4} - \frac{\pi i}{4}\right] \end{aligned} \tag{17}$$

$$A_2 = 0{,}2 + 4{,}7i;\qquad B_2 = 2{,}3 + 2{,}2i;\qquad \gamma_2 = 0{,}8;\qquad \beta_0 = 0{,}5\,.$$

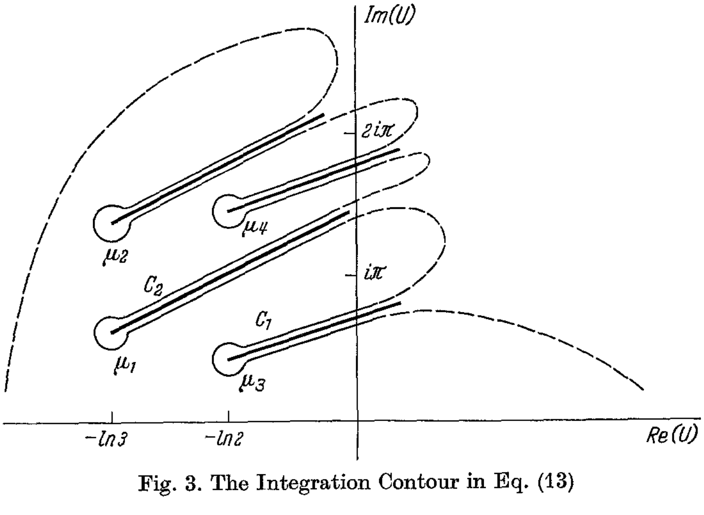

Fig. 3. The Integration Contour in Eq. (13)

Thus for the transition probability we find:

$$P = |I_1|^2 + |I_2|^2 + 2\,|I_1|\,|I_2| \cos(\psi_1 - \psi_2)$$

$$P = 0{,}1 \frac{\omega^2}{\alpha^2 V^2 \lambda^{3/2}} [\exp(-2\lambda\, Im\, A_1) + 8 \exp(-2\lambda\, Im\, A_2) + \tag{18}$$

$$+ 6 \exp[-\lambda\, Im(A_1 + A_2)] \cos(2\lambda - 0{,}3\,\pi)]; \quad Im\, A_1 = 4{,}0; \quad Im\, A_2 = 4{,}7$$

$\xi = 2\lambda$-Massay parameter.

The third term in this formula is a rapidly oscillating interferential term. Its existence is connected with the probability correlation from two ranges of transition.

The corresponding cross-section is:

$$\sigma = 2\pi \int P(V_R)\, \varrho d\varrho \tag{19}$$

$$\sigma = \pi R_0^2 P(V_R) \qquad R_0 \text{ is the same for all the terms}$$

$$\sigma = \sigma^0 + \sigma^1 + \sigma^{01}; \qquad \sigma^0 = 0{,}1\,\pi \frac{\exp(-2\lambda\, Im\, A_1)}{2\alpha^2 \lambda^{3/2}} \tag{20}$$

$$\sigma^{01} = 0{,}6\,\pi \frac{\exp[-\lambda\, Im(A_1 + A_2)]}{2\alpha^2 \lambda^{3/2}} \cos(2\lambda - 0{,}3\,\pi); \sigma^1 = 0{,}8\pi \frac{\exp(-2\lambda Im\, A_2)}{2\alpha^2 \lambda^{3/2}}$$

Here we disregard the slight change of V_R at the points μ_1 and μ_3. This formula should be averaged according to a maxwellian distribution. The integration is made by means of stationary phase method. The computation gives:

$$\sigma^0 = 3 \frac{\exp(-3\gamma_1)^{2/3}}{\alpha^2 \gamma_1^{2/3}}; \sigma^1 = 25 \frac{\exp(-3\gamma_2^{2/3})}{\alpha^2 \gamma_2^{2/3}}$$

$$\sigma^{01} = 18 \frac{\exp(-3\,\gamma_3^{2/3})}{\alpha^2 \gamma_3^{2/3}} \cos(0{,}4\,\gamma_3^{2/3} - 0{,}3\pi) \tag{21}$$

where

$$\gamma_1 = \frac{2\Delta\varepsilon}{\alpha} \sqrt{\frac{\mu}{2KT}}; \gamma_2 = \frac{2{,}4\Delta\varepsilon}{\alpha} \sqrt{\frac{\mu}{2KT}}; \gamma_3 = \frac{2{,}2\Delta\varepsilon}{\alpha} \sqrt{\frac{\mu}{2KT}}$$

The third term in the Eq. (20) has an oscillating character that seems to be due to the method of "modified quantum number" which has been used in the computation of integral (19) [5]. In this approximation the principle of detailed balancing is not fulfilled. The corresponding correction, however, can be easily introduced into the final expression [6].

The Estimation of Cross Sections

$$T = 10^3\,\text{K}^0 \qquad \alpha = 1{,}4$$

1. $\text{Zn}(^3P_1) + \text{Ar}(^1S_0) \rightarrow \text{Zn}(^3P_0) + \text{Ar}(^1S_0) + \Delta\varepsilon\ (190\ \text{cm}^{-1})$

$$\gamma_1 = 3{,}7; \qquad \gamma_2 = 4{,}3; \qquad \gamma_3 = 4{,}0$$

$$\sigma = 1{,}2 \cdot 10^{-19}\ \text{cm}^2 \tag{22}$$

2. $\text{Cd}(^3P_1) + \text{Ar}(^1S_0) \rightarrow \text{Cd}(^3P_0) + \text{Ar}(^1S_0) + \Delta\varepsilon\ (542\ \text{cm}^{-1})$

$$\gamma_1 = 9{,}6; \qquad \gamma_2 = 9{,}7; \qquad \gamma_3 = 9{,}65$$

$$\sigma = 4{,}5 \cdot 10^{-23}\ \text{cm}^2 \tag{23}$$

3. $\text{Hg}(^3P_1) + \text{Ar}(^1S_0) \rightarrow \text{Hg}(^3P_0) + \text{Ar}(^1S_0) + \Delta\varepsilon\ (1767\ \text{cm}^{-1})$

$$\sigma = 1{,}5 \cdot 10^{-31}\ \text{cm}^2. \tag{24}$$

Concluding Remarks

The computation are performed of the non-elastic cross section for transitions between fine structure components of second group excited atoms. The transitions are induced by non-adiabatic interaction with the atoms of inert gas. The numerical evaluation of cross section in the semiclassical approximation is carried out. The corresponding quantum problem can be solved by means of a similar method. However, due to the lack of experimental data, this correction seems to be of no use now. Although the cross sections are small, it should be noted that they seem to be measurable. The minimum cross section measured at present is of the order of $\sim 10^{-21}$ cm^2 (for Cs + He pairs).

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