Radiative Lifetime of the $\nu'1(3P_2)$ States of the HgAr, HgKr, and HgXe Molecules and the Probabilities $A(\nu', \nu'')$ of the $\nu'1(3P_2) - \nu''0^+(1S_0)$ Transitions

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Abstract—A semiempirical method of analysis of quasi-molecular terms in conjunction with experimental potentials of interaction of Hg$(6^3P_1)$ atoms with Ar, Kr, and Xe atoms are used to obtain the Hg$(6^3P_1)$–Ar, Kr, Xe interaction potential, which are applied to calculating the radiative lifetimes of the $\nu'1(3P_2)$ states of the HgAr, HgKr, and HgXe molecules and the probabilities of the $\nu'1(3P_2) - \nu''0^+(1S_0)$ transitions.

Keywords: quasimolecular terms, the interaction potentials, transition probabilities, lifetimes.

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1. INTRODUCTION

To date, the spectra of the transitions from the $A'0^+$ and $B'1$ states to the ground state $X'10^+$ of the HgAr, HgKr, and HgXe molecules, produced by the Hg$(6^3P_1)$ resonance level, are well known (see, e.g., [1–5]). The radiative lifetimes of the $\nu'A'0^+$, and $\nu'B'1$ vibrational states are comparable with the radiative lifetime of the $6^3P_1$ atomic state, since for potential wells with $R > 5\sigma_0$, the dipole moments of the molecular transitions are close to the corresponding value for the atomic transition [6]. In this paper, we investigate the radiative lifetimes of the $\nu'\tilde{c'}1$ state of the HgAr, HgKr, and HgXe molecules. The $\tilde{c'}1$ state (hereinafter denoted as $1(3P_1)$) is produced by the Hg$(6^3P_1)$ metastable level; for it, the transition dipole moment of the transition to the ground state is strongly dependent on the interatomic distance [6]. In the present work, the radiative lifetimes of the $\nu'1(3P_2)$ states and the probabilities of the $\nu'1(3P_2) - \nu''0^+(1S_0)$ transitions were calculated using semiempirical potentials of interaction of Hg$(6^3P_2)$ with Ar, Kr, and Xe [7], the probabilities of the radiative transitions [6], and experimental potentials of interaction in the ground state [4, 8, 9]. In what follows, we outline the main features of the semiempirical method of analysis of quasimolecular terms [9], which makes it possible to determine the interaction potential for the state $1(3P_2)$ and the probability of the $1(3P_2) - 0^+(1S_0)$ radiative transition on the basis of experimental data for the $1(3P_1)$ and $0^+(3P_1)$ states [6].

2. EFFECTIVE HAMILTONIAN AND SEMIEMPIRICAL METHOD OF ANALYSIS OF QUASIMOLECULAR TERMS

To calculate the probabilities of the radiative transitions Hg$(6^3P_2) + X \rightarrow$ Hg$(6^3S_0) + X + h\nu$ (X is an inert gas atom) from bound states in the first approximation, it is sufficient to use the single-configuration approximation. The matter is that the admixture of the wave functions of the overlying configurations of Hg$^+$–X to the wave functions of Hg$(6^3P_2) + X$ under the influence of interatomic interactions is small in this range of distances $R$. The most significant mixing of wave functions occurs in the single configuration Hg$(6s6p)$–X, which gives rise to the Hg$(6^3P_1)$ resonant states, with the highest probabilities of the radiative transitions to the ground state.

That the probabilities of the transitions $\Omega = 1(3P_1)$, $0^+(3P_1) \rightarrow 0^+(1S_0)$ change with the interatomic dis-
tance and the prohibition on the \(1(3P_i) \rightarrow 0^+(1S_0)\) transition is removed as the atoms approach each other is associated with the mixing of the wave functions of the Hg(6s6p)–X configuration due to the interatomic interaction. To determine the degree of mixing of the wave functions of this configuration, we used the effective Hamiltonian method [10] in the formulation of [6, 7, 11]. This formulation, along with the interatomic interaction, takes into account the intra-atomic interactions that lead to the splitting of the levels of the 6s6p configuration and lift the prohibition on the intercombination transition \(6^3P_i \rightarrow 6^1S_0\) in the free Hg atom.

The matrix elements of the effective Hamiltonian \(\hat{H}\) for the \(M(\text{nsnp})–X\) configuration were calculated in [6, 11]. The nonzero matrix elements of the Hamiltonian \(\hat{H}\) in the basis of diabatic quasimolecular wave functions of coupling case \(c\), which are the products of the atomic wave functions \(\psi_{i\sigma}(\hat{1})\),

\[
\left\{ \psi_{i\sigma}(\hat{1}) \right\}_{ic} = \left[ \text{Hg}(6^3P_i) \right]_{ic} \left[ \chi_{(1S_0)} \right],
\]

(1)

\(\left[ \text{Hg}(6^3P_i) \right]_{ic}\) is the atomic wave function for intermediate coupling case \(c\), are presented in the form [6]

\[
\langle \psi_{i\sigma}(\hat{1}) | \hat{H} | \psi_{i\sigma}(\hat{1}) \rangle = E(3P_i) + 3H_{\pi},
\]

(2)

\[
\langle \psi_{i\sigma}(\hat{1}) | \hat{H} | \psi_{i\sigma}(\hat{1}) \rangle = E(3P_i) + a^2H_\sigma + b^2(3H_\sigma + 3H_\pi),
\]

(3)

\[
\langle \psi_{i\sigma}(\hat{1}) | \hat{H} | \psi_{i\sigma}(\hat{1}) \rangle = -b(3H_\sigma - 3H_\pi),
\]

(4)

\[
\langle \psi_{i\sigma}(\hat{1}) | \hat{H} | \psi_{i\sigma}(\hat{1}) \rangle = \frac{ab}{2}(3H_\sigma - 3H_\pi),
\]

(5)

\[
\langle \psi_{i\sigma}(\hat{1}) | \hat{H} | \psi_{i\sigma}(\hat{1}) \rangle = E(3P_i) + \frac{1}{2}(3H_\sigma + 3H_\pi),
\]

(6)

\[
\langle \psi_{i\sigma}(\hat{1}) | \hat{H} | \psi_{i\sigma}(\hat{1}) \rangle = -\frac{a}{2}(3H_\sigma - 3H_\pi),
\]

(7)

\[
\langle \psi_{i\sigma}(\hat{1}) | \hat{H} | \psi_{i\sigma}(\hat{1}) \rangle = E(3P_i) + b^2H_\pi + \frac{b^2}{2}(3H_\sigma + 3H_\pi),
\]

(8)

\[
\langle \psi_{i\sigma}(\hat{1}) | \hat{H} | \psi_{i\sigma}(\hat{1}) \rangle = E(3P_i) + a^2H_\sigma + b^3H_\pi,
\]

(9)

\[
\langle \psi_{i\sigma}(\hat{1}) | \hat{H} | \psi_{i\sigma}(\hat{1}) \rangle = -ab(3H_\sigma - 3H_\pi),
\]

(10)

\[
\langle \psi_{i\sigma}(\hat{1}) | \hat{H} | \psi_{i\sigma}(\hat{1}) \rangle = E(3P_i) + b^2H_\sigma + a^3H_\pi,
\]

(11)

\[
\langle \psi_{i\sigma}(\hat{1}) | \hat{H} | \psi_{i\sigma}(\hat{1}) \rangle = E(3P_i) + \frac{2}{3}H_\sigma + \frac{1}{3}H_\pi,
\]

(12)

where \(L\) and \(S\) are the potentials of interaction of the Hg(61P) and Hg(63P) atoms with the X atom in the \(1^3\Sigma\) and \(1^3\Pi\) states without regard for the spin–orbit interaction in the Hg(6s6p) atom; \(E(1^3P_i)\) is the energy of the \(1^3P_i\) atomic levels, \(a\) and \(b\) are the amplitudes of the expansion of their atomic eigenfunctions for the intermediate coupling case in the wavefunctions for the \(LS\) coupling case:

\[
\left[ \text{Hg}(1^3P_\Omega) \right]_{ic}^{at} = a \left[ \text{Hg}(1^3P_\Omega) \right]_{LS}^{at} + b \left[ \text{Hg}(3^3P_\Omega) \right]_{LS}^{at},
\]

(15)

\[
\left[ \text{Hg}(3^3P_\Omega) \right]_{ic}^{at} = -b \left[ \text{Hg}(1^3P_\Omega) \right]_{LS}^{at} + a \left[ \text{Hg}(3^3P_\Omega) \right]_{LS}^{at},
\]

(16)

\[
\left[ \text{Hg}(3^3P_\Omega) \right]_{ic}^{at} = \left[ \text{Hg}(3^3P_\Omega) \right]_{LS}^{at}.
\]

(17)

\[
\left[ \text{Hg}(3^3P_\Omega) \right]_{ic}^{at} = \left[ \text{Hg}(3^3P_\Omega) \right]_{LS}^{at}.
\]

(18)

In the calculations, we used the approximate values of the amplitudes, \(a = 0.979\) and \(b = -0.203\) [11].

In the analysis of the interaction potentials and probabilities of radiative decay for the Hg(63P)–X triplet states, we can set in the first approximation \(H_\sigma = 3H_\pi\) and \(H_\mu = 3H_\pi\) [6, 7]. In this approximation, the dependences \(3H_\pi(R)\) and \(3H_\sigma(R)\) for the interactions Hg(63P) with Ar, Kr, and Xe determined in [7] within the framework of a semiempirical analysis of the quasimolecular terms by comparing the available experimental spectroscopic data for the interaction potentials in the 1(3P_i) and 0(1^3P_i) states with the corresponding eigenvalues of effective Hamiltonian matrix (2)–(14). The resulting \(3H_\pi(R)\) and \(3H_\sigma(R)\) dependences made it possible to determined [7] semiempirical interaction potentials for the 0^−, 1, 2(3P_2) and 0^−(3P_0) as the eigenvalues of matrix (2)–(14).

The results reported by different authors for the interaction potentials for the 1,0(3P_2) states differ somewhat from each other. Therefore, using data from different works, the authors of [7] constructed two versions of semiempirical terms for each of the HgAr, HgKr, and HgXe molecules. In the present work, we use version \(a\) of semiempirical potential for HgAr and